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WADC TECHNICAL REPORT 54-98

INVESTIGATION AND DEVELOPMENT OF HIGH TEMPERATURE
STRUCTURAL ADHESIVES

H. N. HOMEYER, JR.
J. H. PRESTON
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THE CONNECTICUT HARD RUBBER CO.

FEBRUARY 1954

WRIGHT AIR DEVELOPMENT CENTER

Incl. 1

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HIGH TEMPERATURE STRUCTURAL ADHESIVES

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The Connecticut Hard Rubber Company

February 1954

Materials Laboratory
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Wright Air Development Center
Air Research and Development Command
United States Air Force
Wright-Patterson Air Force Base, Ohio

FOREWORD

This report was prepared by The Connecticut Hard Rubber Company on Air Force Contract No. AF 33(616)-427. The contract was initiated under Research and Development Order No. 582-218, "Hot Cycle Pressure Jet Rotor Assembly," and was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with Lt. Arthur J. Butler, Jr. acting as project engineer.

The authors wish to acknowledge the contribution made by E. J. McPartland and J. J. McCarthy, laboratory technicians, who carried out, in a most satisfactory manner, a large part of the experimental work.

ABSTRACT

This report describes work on the investigation and development of structural adhesives from silicone materials for high temperature service conditions such as are encountered in certain aircraft operations. The results of lap-shear tests on aluminum-to-aluminum specimens bonded with a large number of silicone resins, rubbers, copolymers, and experimentally compounded mixtures are reported. The data presented shows that adhesives with considerable strength can be obtained and that the target objectives, although not yet reached, are not beyond the realm of possibility. It was found that shear strengths averaging over 2000 psi at 70°F, 700 to 900 psi at 300°F, and 400 psi at 500°F, can be obtained with unmodified resins.

The research was carried out by personnel of the Connecticut Hard Rubber Company during the period from 15 January 1953 to 15 January 1954.

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INTRODUCTION

The technology of adhesives of all types has progressed very rapidly in recent years. One of the most striking advances has been in the metal-to-metal adhesives. In the case of the lighter metals, it is now possible to obtain stronger joints with adhesives than by any other methods. In many cases, the joints are as strong as the metal itself. For example, welding is not feasible for many aluminum alloys because it reduces the strength of the weld area from as high as 75,000 psi down to that of annealed aluminum, about 5,000 psi. Riveting has several serious drawbacks: high labor cost, uneven skin surface at the rivet head, and very poor resistance to vibration due to stress concentration around the rivet holes.

It has been possible to fabricate certain types of structures such as honeycomb sandwich constructions which would not be feasible by any other method. Some of the parts such as helicopter blades, previously made by riveting, are now made entirely by means of structural adhesives with great improvement in service life. The average useful life of such a blade has been increased from 90 hours with rivets to over 1200 hours when adhesives were adopted, because of the improved vibration resistance in the thin trailing edge of the blade. The use of structural adhesives is spreading. Large sections of aircraft, such as portions of the wings of the B-36 bomber, are now being assembled by this means. The resulting smoother skin surface considerably reduces drag.

One characteristic of structural adhesives that is a handicap for some applications is their thermoplastic tendency. To a greater or less degree, all the structural adhesives in commercial use soften at high temperatures and lose strength. Furthermore, since nearly all are organic in nature, they will all undergo decomposition at high temperatures. These limitations are quite serious in the case of the supersonic aircraft and guided missiles now going into production.

In the new design of helicopters, the main engine is a gas-turbine type located in the fuselage, whose exhaust is led through the hollow blades to after-burners at their tips. The blade temperatures reach 400°F in this case and since no suitable adhesive is available it became necessary to go back to riveted construction.

Several research and development contracts have been aimed at improving the high temperature performance of structural adhesives. There are two still in progress. One concerns the use of epoxide-phenolics; the present one covers the silicone polymers. It is felt that the inherent high temperature stability of the silicones justified a major effort in developing a satisfactory adhesive based on them.

The work to date has shown that adhesives with considerable strength can be obtained and that the target objectives, although not yet reached, are not beyond the realm of possibility. Many types of improvements which have suggested themselves in the present work are worthy of further investigation.

I. SUMMARY

- A. A screening program of all commercially available silicone resins as potential structural adhesive materials has revealed that:
1. Shear strengths averaging over 2000 psi at 70°, 700 to 900 psi at 300°, and 400 psi at 500°F can be obtained with unmodified resins.
 2. Of all the resins, Dow Corning 2103 has given the best shear test performance at elevated temperatures, with General Electric 81397 and Dow Corning 2106, 804, XR-100 and XR-544 next best. Dow Corning 1360, 996, and General Electric 81390 have given the highest shear test values at 70°F. Many other resins show good shear strength (more than 1200 psi) at 70°F.
 3. Reduced shear strengths at elevated temperatures are caused by thermoplasticity rather than by decomposition.
- B. A study of certain silicone-organic copolymers has shown that silicone-alkyds and epoxies produce strong aluminum-to-aluminum bonds at moderate temperatures. They have the drawback of being thermoplastic, the same as the pure silicones do.
- C. A study of fillers and polymerization catalysts as modifiers for silicone resins and copolymers has shown improvement in elevated temperature shear strengths in some cases. Tetra butyl titanate and tetra isopropyl titanate were the most effective catalysts. Aluminum dust, Celite, Santocel, and Titanium dioxide fillers improved shear test values in some particular cases.
- D. Evaluations of commercially available silicone rubber-based adhesives have shown Dow Corning's X6719-A to give the highest shear strength in bonding aluminum - over 700 psi at 70° and 200 psi at 500°F.
- E. An initial study of mixtures of silicone resins with silicone rubbers as structural adhesives has indicated that there is little value in such mixtures.
- F. Extensive evaluations of primers and metal surface treatments such as anodizing in preparation for bonding

with both resins and rubbers has resulted in shear strengths about equal to control samples. In some instances, Connecticut Hard Rubber's 260, silane primer, and Dow Corning's 796, containing orthosilicate, were beneficial for bonding with X 6719-A. In one case, anodizing aluminum surface to be bonded brought improvement in a silicone resin bond.

II. OBJECTIVES, PROGRAM, and RECOMMENDATIONS

A. Objectives of the Contract

The object of the contract is to provide a structural adhesive for metal-to-metal joints for long-time service at elevated temperatures, specifically for 1200 hours at 500°F (or higher) and for shorter time service at 700°F (or higher). The adhesive shall be suitable primarily for stainless steel and, secondly, aluminum alloys and titanium alloys. In order to obtain the requisite strength, the following requirements must be met:

1. Shear Strength.

- a. Room Temperature - 2500 psi minimum is desired. However, a lower room temperature strength is acceptable if the elevated temperature target is attained.
- b. Low temperature (-70°C) - 2500 psi. However, the low temperature strength may be lower as specified in (a) above.
- c. 500°F continuous temperature - 1000 psi minimum when tested at 500°F after 1200 hours at 500°F.
- d. 500°F cycling temperature - 80% of the strength in (c) above when tested at 500°F after 100 cycles between 500°F and room temperature (with 200 hours cumulative time at 500°F).
- e. 700°F - 1000 psi when tested at 700°F immediately upon reaching 700°F from room temperature.
- f. Exposure to water and salt spray - 80% of original room-temperature strength when tested at room temperature after exposure to water or to salt spray for 30 days.
- g. Exposure to chemicals - 80% of original room-temperature strength after exposure for seven days at room temperature to ethylene glycol, to anti-icing fluid, to hydraulic oil and to hydrocarbon fluids.

2. Creep Strength.

Under static continuous loading at 500°F, a stress of 500 psi shall be supported for 1200 hours without failure of the tensile lap joint. The adhesive shall not be brittle under these conditions.

3. Vibration Resistance.

The adhesive shall be particularly adaptable for structures subjected to alternating loads. It shall withstand an axial loaded tensile fatigue test on lap joints at 0 to 500 psi for at least 10⁷ cycles (3600 per minute) at a temperature of 500°F.

4. Method of Bonding.

- a. Pressure - A maximum pressure of 50 psi shall be required to establish the bond.
- b. Temperature of application - The adhesive shall be suitable for application to the metal at room temperature.
- c. Time and temperature of curing - The adhesive shall be capable of curing in less than one hour at a temperature of 350°F or less under pressure.
- d. After-curing - After-curing may be used, although it is not preferred.
- e. Suitability for production - The methods of preparation and use of the adhesive shall all be suitable for production techniques.

5. Physical Composition of the Adhesive.

- a. Preferred form.
 - (1) Tape or film (unsupported or supported)
 - (2) Liquid or solution
 - (3) Hot melt or other form.
- b. The shelf life should be at least six months at 80°F.
- c. Pot life - four hours minimum.
- d. The adhesive shall preferably be a one-part adhesive, but two or more part adhesives are acceptable.

B. Evaluation Procedure

1. Screening Test Procedure

Numerous adhesive formulations are required to be developed and evaluated. These cannot all be tested for all the desired properties. Therefore, screening tests must be adopted and the following screening test procedure is followed:

- a. Metal - 0.064 inch 4S-T3 Alclad aluminum. Use precut aluminum panels, 1 inch by 4 inch with $\frac{1}{2}$ inch lap joint.
- b. Measure room-temperature shear strength.
- c. Test shear strength after reaching 500°F from room temperature.
- d. Test shear strength at 500°F after 200 hours' exposure at 500°F.

2. Final Test Procedure.

- a. Metal - 0.036 to 0.040 inch thick, 18-8 full hard stainless steel.
- b. Size of panel - 4 inches long by 4 inches wide. Over-lap, $\frac{1}{2}$ inch. Cut panels into strips, one inch wide, after bonding.
- c. Tests required:
 - (1) Room-temperature shear strength
 - (2) Shear strength immediately after reaching 500°F
 - (3) Shear strength at 500°F after 200 hours of unstressed exposure to 500°F.
 - (4) Shear strength at 500°F after 1200 hours of unstressed exposure to 500°F
 - (5) Salt spray resistance - retention of shear strength after 30 days' exposure at room temperature.
 - (6) Creep strength - exposure to temperature of 500°F for 200 hours, followed by static loading at 500 psi for 200 hours at 500°F.
 - (7) The most successful adhesives under (6) above shall be loaded for 1200 hours under these conditions.

C. Recommendations:

The results obtained to date are sufficiently promising that it is recommended that:

1. The research and development on silicone resin-based materials for structural adhesives be continued.
2. The effect of structural variation in silicone resin molecules on the properties of the polymer be thoroughly investigated in literature and laboratory in a program aimed at "tailor-making" a polymer for a high-temperature service structural adhesive.
3. Extensive studies be made of isocyanates, high-temperature phenolics, epoxies, and alkyds in combination or in copolymers with silicone resin for structural adhesives.
4. Studies be made of the value of mixing silicone resins for structural adhesives. Evidence has been seen for possible advantages in such mixtures.
5. The silicone resin constituents of silicone molding compounds which are not thermoplastic at 500°F be investigated.
6. Careful studies be made of the effects of the best catalysts and fillers (from the screening experiments reported at this time) on the shear strength of the best resins, copolymers, and mixtures from (4) above.
7. The value of chelates in reducing thermoplasticity of the silicone resins be determined.
8. The evaluation of new products such as polymers, copolymers, filler, catalyst and metal surface treating materials be continued as they become available.
9. As promising polymers, mixtures, and compounds are developed out of the contract research, they be subjected to aging tests at 500°F and that the remaining properties be determined in accordance with the contract.

III. LITERATURE SURVEY AND BACKGROUND INFORMATION

A. Structural Adhesives - Presently in Use¹

There are many practical metal adhesives available at the present time. The first successful formulations for this use were the phenolic-vinyl copolymers. These are sold under the names of Redux by Resinous Products Chemical Company and FM-47 by Bloomingdale Rubber Company, and Plycozite. Although theoretically a thermosetting polymer, the vinyl resin, which was used to act as a built-in plasticizer for the phenolic resin, caused the adhesive to be very thermoplastic and have objectionable loss in strength above 165°F. The next type of adhesive is the group of phenolic-neoprene copolymers. These are sold under the trade name of Cycleweld by Chrysler Corporation, Metlbond by Narmco Corporation, Reanite by U.S. Stoneware Corporation and Plastilock by B. F. Goodrich Corporation. These materials are considerably less thermoplastic than the former but were deficient in aging characteristics. The next group of phenolic copolymers were the phenolic-Hycar or acrylonitrile rubber polymers. They were sold under the trade names of GS-29 by Naugatuck Chemical Company, PA-101 by Bloomingdale Rubber Company and Enrup. Epoxide resins developed by Ciba Ltd. in Switzerland and sold under the trade name of Araldite are also manufactured by The Shell Chemical Company and sold under the trade name of Epon. They are produced from epichlorohydrin and bisphenol.

The vinyl-phenolics give some of the most successful structural adhesives. Their shear strength, although satisfactory, is not outstanding, but they are thoroughly reliable in production and are being used commercially in such applications as helicopter blades. Their outstanding drawback is their lack of high-temperature strength. The other phenolic modifications such as with neoprene and Hycar have certain drawbacks which have limited their commercial applicability. The epoxide adhesives develop high shear strength and retain their strength up to 200° or 250°F.

B. Surface Preparation Methods for Laboratory Testing

The proper preparation of the surfaces for the use with various structural adhesives has been the subject of intensive investigations by many workers. The preparation methods are quite specific for each metal and must be followed rigorously in order to obtain optimum and reproducible results.

1/Air Force Tech. Report 5896-1

1. Aluminum

There are several different procedures which have been satisfactorily utilized for aluminum, which include chromate treatment, caustic solution treatment, and anodizing. In all of these methods, the metal test specimen is first immersed for an extended period of time, usually overnight, in a solution of trichloroethylene at room temperature. This serves to remove grease and to present a clean surface for the chemical treatment which follows.

The chromate treatment is usually accomplished by immersing the specimens to be treated for ten minutes in a solution of 25% sulphuric acid containing 2½% by weight of sodium dichromate. The solution is maintained at a temperature of 150° to 160°F.

Anodizing consists of forming a thin layer of hard, corrosion-resistant, non-porous aluminum oxide on the surface of the aluminum. This can be accomplished either electrolytically or chemically. The electrolytic method consists of degreasing the aluminum surface as above, cleaning in a sodium hydroxide solution (¼ lb per gallon) for 30 seconds at 160°F, followed by dipping in a nitric acid solution of 60% for 30 seconds at room temperature. The metal is then connected to electrical anodes and dipped in a 15% sulphuric acid solution at 85°F. The voltage is slowly raised to 18 volts in a period of five minutes and then maintained at 18 volts for forty-five minutes with a current density of 20 amperes per square foot. This produces a highly porous layer of aluminum hydroxide on the surface of the aluminum, which can then be converted to the aluminum oxide form by dipping in a boiling water solution for about 30 minutes, a process known as sealing. During the sealing operation, the aluminum hydroxide film splits off water to form a tightly adhering layer of aluminum oxide monohydrate. The chemical anodizing method produces a similar end result, but the chemical techniques employed have not been disclosed in detail.

2. Stainless Steel

Technical note WC TR 53-148 lists a number of experiments in evaluating surface preparation methods for stainless steel for use with epoxide-phenolic structural adhesives. Although the results were not conclusive, strengths as high as 150% of the strength on prepared aluminum panels were obtained. the most satisfactory method consisted of dipping, after

degreasing, into the following solutions, with rinse between each step:

- a. 10% H_2SO_4 plus 10% HCl at 130° to 140°F for 10 minutes.
- b. A solution of 6% H_2SO_4 , 6% HF , 2.2% CrO_3 heated from room temperature to 140°F.
- c. 50% HNO_3 one hour at room temperature.

Another method which has been used successfully consists of dipping in:

- a. 15% by weight HCl for five minutes at 80°F.
- b. 30% by weight HNO_3 for thirty minutes at 80°F.

3. Titanium

Two different procedures were found to be satisfactory for titanium. The first consisted of dipping for ten minutes in 10% aqueous hydrofluoric acid at room temperature. The second method consisted of dipping in:

- a. 10% aqueous HF for one minute at room temperature.
- b. 50% HNO_3 for one half-hour at room temperature.

Other procedures, such as anodizing and the use of concentrated hydrochloric acid and sulphuric acid, were inferior to the hydrochloric acid treatment.

C. Adhesives Under Development

Shell Development Company has a contract for the investigation of epoxide adhesives. Their optimum composition to date consists of an epoxide-phenolic resin mixture using aluminum dust as a reinforcing filler. The composition is as follows:

Parts by Weight

Epon 1001	33
Plyophen 5023	67
Aluminum dust (CF300 mesh)	100
Dicyandiamide	6

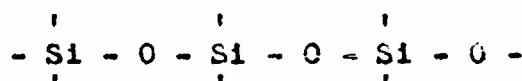
This cured at 330°F for forty-five minutes at a pressure of 26 psi.

The other materials under investigation are the silicone polymers, both resin and rubber, which are the subject of this investigation.

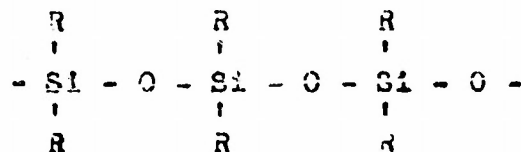
D, The Basic Chemistry of Silicone Polymers

1. The Siloxane Chain

The silicones are a unique class of polymeric materials which contain both inorganic and organic substituents in the same molecule. The skeleton structure of the polymers is inorganic in nature and consists of silicon atoms joined by oxygen atoms:



The organic portions of the molecule are affixed to the residual valences of the quadrivalent silicon atom:



The exceptional stability of the silicones to thermal and oxidative decomposition is attributed to the inorganic skeleton of the polymers. This skeleton is far more stable than those of the analogous organic polymers.

2. History of the Silicones

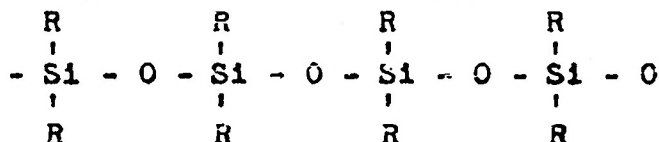
The silicones, despite their rather recent commercial debut, have been known for many years. F. S. Kipping, a celebrated English chemist published a voluminous series of papers on the chemistry of silicon compounds in the period 1890-1937. He coined the term "silicone" because of the rather tenuous similarity between an organic ketone $\text{R}_2\text{-C}=\text{O}$ and the organic silicone $\text{R}_2\text{-Si}=\text{O}$. Kipping was disappointed because he was never able to get nice clean, sharply melting crystals like those which are customarily obtained in organic chemistry. All he could get was various types of oils and amorphous solid powders. One of the first chemists to realize the value of the silicone polymers was a Russian, Andrianov, who did considerable work on the silicone resins. A large amount of research work, followed by pilot plant and production work, on silicone resins was accomplished in this country just prior

to World War II. The silicone rubber polymers did not appear commercially until after the end of World War II.

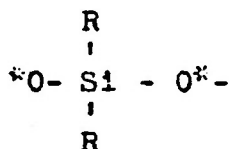
3. Functionality

By strict definition there must be two organic groups per silicon-oxygen atom pair in a silicone. This is commonly expressed as $R/Si = 2.0$, where R represents an organic group. However, it is not necessary from a chemical standpoint that the ratio be held to 2.0 and the term "silicone" has been broadened to include all the compounds of this type, regardless of the ratio of organic groups to silicon-oxygen pairs.

In the silicone system, it is always necessary that the polymer be built up from a silicon-oxygen chain:

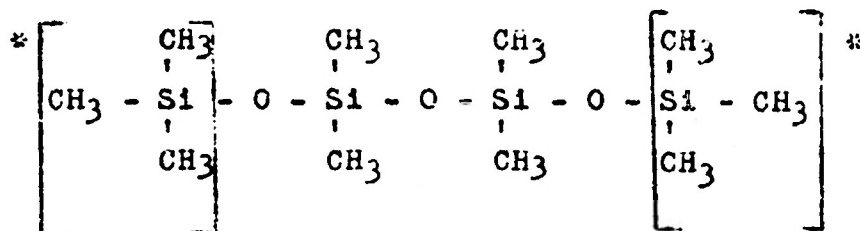


When both of the groups represented by the letter "R" are organic ones ($R/Si = 2.0$), then the monomer from which it is formed is termed "difunctional", i.e. it has two functional oxygen atoms*:

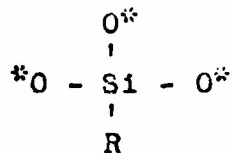


The monofunctional units cannot form chains since a dimer is the largest possible combination of two monofunctional units. Their principal purpose is to act as "chain stoppers" which prevent further polymerization from occurring at elevated temperatures.

Following is a difunctional chain stopped at both ends by monofunctional groups*:



When one of the groups represented by the letter "R" is not an organic one, but rather an oxygen

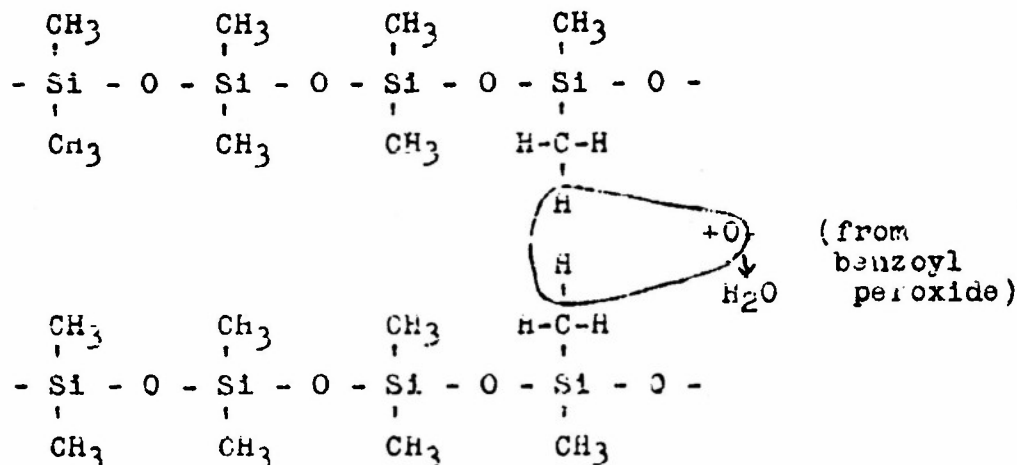


then $\text{R/Si} = 1.0$, and the group is called trifunctional*.

4. The Silicone Rubbers

The most widely known commercial silicone polymers are comprised of difunctional units combined in molecules of various chain lengths. A large volume of literature has been published on these materials. By far, the most important difunctional units are those which have methyl groups. When the chain length is relatively short, the materials are oil-like in their physical characteristics, and such polymers, properly "chain-stopped", form very stable, excellent lubricating oils for extremely high-temperature service.

As the chain length is increased, the viscosity of the fluids increases proportionately, and when the chain length has reached about 1000 units, a rubber-like material can be made from the polymer. However, the plain polymer is not rubber-like by itself, but rather is an extremely viscous fluid which flows slowly and conforms to the shape of the container at ordinary temperatures. In order to develop rubber-like characteristics, it is necessary to add a reinforcing filler, such as finely divided silica, and a vulcanizing agent, such as benzoyl peroxide. It is thought that the polymer molecules coat the larger filler particles, thus greatly changing their flow behavior. The vulcanizing agent serves to oxidize the hydrogen atom from the methyl group of each of two adjacent chains to form an ethylenic bridge between them, and by this means rubber-like characteristics of commercial utility can be obtained. It should be noted that the vulcanization reaction does not increase the chain length; the polymer chains are full length before curing.



The ordinary commercial silicone rubbers today are pure dimethyl silicone polymers. In the past, some polymers had been offered which contained a certain proportion of trifunctional units which served to cross-link the chains by means of oxygen bridges. Although the unvulcanized polymers of this type much more closely resembled natural rubber, it was found that the properties of the vulcanized materials were inferior to the straight difunctional polymer, and much poorer tensile strength stocks resulted from it.

The freezing-point temperature of a strictly difunctional polymer is approximately -60°F , and this places a temperature limit on the serviceability of the material. It has been found that by substituting phenyl groups in place of methyl groups in rather random fashions at intervals along the chain, the symmetry of the structure is disturbed and steric hindrance results, which prevents adjacent chains from aligning themselves as closely together, and thus reduces the crystallization temperature to a much lower point, about -110°F .

5. The Silicone Resins

The literature on the trifunctional polymers, known as resins, is much less extensive than on the difunctional. The trifunctional polymers are very different in their physical properties. Since they have three oxygen atoms on varying proportions of units, they not only can link up in one plane as the difunctional units do, but they can form a three-dimensional network quite analogous to the thermosetting resins, e.g. "Bakelite." A completely trifunctional silicone polymer closely resembles silica and forms hard, brittle, glass-like

materials upon complete curing. In the case of the phenyl type trifunctional polymer, the cured material is so brittle that it cannot be used commercially. In the case of the methyl type, it can be used for certain purposes, but has serious limitations because of its extreme brittleness. The ordinary commercial silicone resins consist of a mixture of difunctional and trifunctional units. By this means, it is possible to incorporate some of the rubber-like characteristics of the difunctional materials with the hardness and high-temperature stability of trifunctional materials.

The relative proportion of methyl to phenyl groups in the silicone resin is another major variable. By a proper selection of these various constituents, a very wide selection of polymers can be obtained, and the resins which are commercially available range from very flexible, almost rubber-like materials, on the one hand, to hard, brittle, glass-like on the other, with types of all degrees in between.

One of the major difficulties of the synthesis of silicone resins is that they require both difunctional and trifunctional units in more or less orderly arrangement along the chains to develop optimum physical qualities. However, the trifunctional units are very much more reactive than the difunctional and consequently react with each other in preference to the lethargic difunctional units. They form ring structures in this manner and effectively remove themselves from reaction with the difunctional units. Thus, instead of a uniformly arranged mixture, the resin becomes rather large islands of hard resin masses dispersed in a soft thermoplastic difunctional rubber-like material. When viewed in the aggregate, the resins are therefore not as thermosetting as they should be, but soften considerably at higher temperatures.

The trifunctional polymers are cured by a different mechanism than the difunctional rubber-like polymers. It was shown that the latter are cured by the formulation of ethylenic linkages by oxidation of a pair of methyl groups on adjacent chains. The trifunctional resin systems are cured by a condensation reaction which involves splitting off water between a pair of hydroxyl groups. The resin catalysts which are most effective are materials such as triethanolamine, zinc and iron octoates and naphthenates etc. which are effective in various condensation reactions. The ultimate properties of the cured resin as well as the rate of curing are markedly influenced by the catalyst employed. In contrast to the rubbers which are initially long chain, high-molecular-weight polymers which only cross-link during curing, the resins are relatively low-

molecular-weight materials which cure by a condensation process that greatly increases their molecular size.

In addition to methyl and phenyl siloxane polymers which are the two classes most widely offered commercially, a very large number of silicone polymers containing other organic groups have been synthesized in the laboratory and a few have been offered commercially, but they have found only very limited acceptance. A rubber-like polymer comprised of ethyl silicone can be made. It has excellent rubber-like properties, but has the very serious drawback that the ethyl group possesses greater high-temperature sensitivity than the methyl group. At temperatures above 300°F, the polymer decomposes. Another polymer which has been used for certain specialized purposes is the vinyl silicone. This has been found to increase adhesion of silicone rubber and silicone resins to glass fabrics.

E. Properties and Processing of Silicone Polymers for Structural Adhesives

A large amount of technical information pertaining to the processing and characteristics of silicone polymers has been gradually accumulated. The information which follows, not readily available from basic chemistry sources or manufacturers' data sheets, has been incorporated into the experimental program.

Particular attention has been paid to methods of improving the strength, high-temperature stability, and adhesion of the polymers to metal surfaces. These deficiencies in the materials examined have been the chief weak points in experimental structural adhesive bonds. The information covered in the following sections is pertinent to the improvement of these properties.

1. Composition of Polymers

Most of the silicone resins on the market today fall within the range of the two types of composition variables discussed in the previous section. They are differentiated one from another in the proportions of methyl and phenyl organic groups on the one hand, and by the R:Si ratio on the other. The R:Si ratio represents indirectly the proportions of difunctional and trifunctional monomers present, and hence, the ultimate cross-linking potential.

General Electric Company, Dow Corning Corporation, and Linde Air Products Company are the chief manufacturers of silicone polymers - both elastomers and resins. Two major composition variables are changed in each commercial polymer to suit the intended application. The numbering systems employed by the manufacturers are often a direct key to the properties of the silicone resin. In the General Electric SR series numbering system, in general, the flexibility ranges from the greatest flexibility in the lowest numbers, SR-17, 28 and 32, to the least flexibility in the highest numbers, SR-80, 82, 98 and 02 (taken as 102 in the series). Similarly, the curing requirements range from the slowest curing in the lowest numbered resins to the fastest curing in the highest numbered resins. This would indicate the likelihood that, in a general way, the degree of difunctionality versus trifunctionality would range from the least trifunctional in the low-numbered resins to the most trifunctional in the high-numbered resins. Of course, the curing requirements are also affected by the catalyst which is included in some of the resins. There is no direct connection between the phenyl content and the numbering system, but it is known that the specific gravity increases as the phenyl content increases.

Dow Corning employs a numbering system whereby each group of resins, such as the 800 series or the 900 series, is intended for a certain end use such as bonding, protective coatings, or as electrical insulating varnishes. Within a series, the flexibility is said to range from the most flexible at the lower end to the least flexible at the upper end of the series.

Regarding the compositions of particular resins, both SR-80 and DC-804 are known to be all-methyl resins, that is, all the organic groups are methyl ones. It is assumed that most of the remaining resins contain a proportion of phenyl groups. SR-32 and SR-17, resins with good flexibility, are known to contain phenyl groups. SR-80 is the most compatible of the SR resins with other silicone materials (most silicone resins are incompatible with silicone elastomers). SR-82 is the most compatible of the SR series with non-silicone materials, and is widely used for blending with alkyd and melamine resins in the manufacture of paints and enamels.

In the Linde resin series, X-61 has the largest proportion of difunctional groups, is consequently the most flexible and is also the most heat-stable. X-62 is faster curing and also heat-stable. X-63 is fully condensed, containing only about 2% residual free OH groups, and is said to be similar to SR-32 which contains phenyl groups. Linde also supplies

polyethoxy silanes in the X-14 series, which are intermediate materials for resin polymerizations. They are hydrolyzable and are used within that company to make soluble resin products. They differ from each other in the proportion of methyl and phenyl groups. X-14A is 100% phenyl ethoxy silane, X-14C is 100% methyl and X-14B is 50% methyl, 50% phenyl ethoxy silane.

The difunctional silicone polymers (rubbers) vary also in the methyl versus phenyl content. General Electric's SE-76 is an all-methyl polymer and is most widely used for general service purposes. SE-51 contains a percentage of phenyl groups, and is intended particularly for low-temperature service, which is obtained at the slight expense of some other physical properties. It may be of value in the development of potential structural adhesives from mixtures of resin and rubber because it is inherently more compatible with resins containing phenyl groups than are the all-methyl rubbers. SE-79 contains some trifunctional groups which provide oxygen linkages between the chains in addition to the regular ethylenic linkages of difunctional rubbers. It can be considered to be similar to a copolymer of resin and rubber. SE-79 is polymerized in an acid medium (ferric chloride), whereas SE-51 and SE-76 are thought to be produced in an alkaline medium.

2. Catalysts

The catalysts for resin polymerization are the types which permit condensation reactions. The most widely used is triethanolamine, which is a very rapid catalyst and produces hard, brittle resins. Various metallic salts, such as octoates and naphthenates of lead, zinc and iron are widely used. Cobalt and manganese salts are sometimes used, but they, like iron salts, although efficient, cause bad staining. The lead and tin salts produce rapid gelation but have almost no effect on the final cure. They do not reduce the high-temperature resistance of the cured polymer. They are useful as auxiliary catalysts with triethanolamine to prevent the resin from liquifying during the cure and running out of the glue line. Zinc salts are slow acting and have the least deleterious effects on the final resin. Iron salts produce great hardness but reduce the ultimate heat-stability.

The catalyst used has a considerable effect on the adhesion of the resin to metals (Section III, E-7).

Regarding the catalysts in particular resins, it is known that DC-2105 contains a tin salt and that DC-2104 contains two

catalysts: lead 2-ethyl hexoate, and dibutyl tin diacetate both dissolved in n-butanol.

Recent patents ¹ have pointed out the effectiveness of alcohol titanates as resin catalysts. Tetra-butyl Titanate, in particular, has been mentioned.

3. Fillers

A number of fillers have been used successfully with the silicone resins. Large proportions of fine fillers, such as Celite and Santocel C, have been used to advantage in molding powders for silicone dielectric materials of high heat-resistance. Small quantities of these fillers are advantageous in overcoming the limitations of uncompounded resins. They can improve bond strength by increasing the tensile strength as much as three to five times, increasing the stiffness, and lowering the elongation. Aerosil fillers have also been said to increase the strength of resins. It has been suggested that the addition of Santocel C or mica dust would improve the high-temperature properties of resins.

The addition of fillers to silicone elastomers has made useable rubber compounds of them. Fillers can undoubtedly improve the silicone rubber bonding materials. It has been suggested that the bond strength of X-6719A adhesive and SE-51 would be increased by the addition of GS-Silica, the hydrophobic silica pigment produced by Durez. The addition of a small amount of red iron oxide can add 100°F to the upper operating temperature limit of the General Electric silicone elastomers. Fine particles of Teflon and Alon used as fillers can improve the tear and cut growth resistance of elastomers such as X-6719A adhesive. The type of pigment used definitely affects the adhesion to metals. Titanium dioxide is thought to produce the best adhesion.

4. Plasticizers

It may become desirable to plasticize a silicone resin structural adhesive to increase the resistance of the bonds to vibration under operating conditions. Methyl phenyl silicone fluids have been suggested for this purpose because of their relatively greater compatibility with the silicone resins. Such materials as DC-550 and DC-710, which are chain-stopped oils and very heat-stable, might be advantageous. Resin SR-32 would probably be the most compatible with these, and SR-98 the least.

¹/Belgian patent No. 500,963
United States patent No. 2,512,058

5. Other Polymers and Copolymers

The use of vinyl silicones as primers has been suggested since they have been successful in increasing the adhesion of polyesters etc. to glass cloth. The use of ethyl polymers, although possibly advantageous from an adhesion standpoint, has the definite limitation of inferior high-temperature oxidation resistance.

Copolymers of silicone resins with cyanurates and epoxies show theoretical promise for improving adhesion. An evaluation of a new resin comprised of vinyl silicone cross-linked with styrene has been suggested (Linde Y-1043 and 1044). This material is said to have a minimum content of volatiles, and reportedly has good high-temperature stability.

In the case of silicone rubber-resin copolymers, some people in the field would have felt that inferior strength would be obtained, and that the materials would be cheese-like. It was suggested that physical blends of rubber and resin would be more promising than copolymers.

6. Curing

A general observation has been made that industrial curing cycles for resins are inadequate. In most cases, the resins are cured only to a tack-free condition. For example, when a time of four hours would be required to produce optimum properties, frequently only 30 minutes' oven cure is given.

The curing cycles required by silicone resins cover a wide range of temperature and time. In their technical data sheets, General Electric recommends cures in the range from 300° to 500°F and mentions curing times anywhere from five minutes to 48 hours. The longest curing cycle mentioned is for SR-02 (16 to 48 hours at 329° or 6 to 8 hours at 400°F). The shortest cure mentioned is five minutes at 392°F for SR-80 when zinc octoate catalyst has been added.

Dow Corning mentions cures from 275° to 480°F. Recommended times range from thirty minutes to sixteen hours. In several cases, stepwise curing cycles are recommended. For example, for LC-993, a flexible resin, one to three hours at room temperature, plus two to four hours at 275°F plus four to eight hours at 480°F is suggested.

General Electric has developed two experimental resins, 81369 and 81397, to overcome the objectionably long curing cycles usually required by resins. These two cure very rapidly and have excellent heat-stability but have the disadvantages of

being very brittle, having poor adhesion to metal, and foaming during the cure.

7. Primers and Adhesion to Metals

In a comparative study between silicone resins and alkyd resins as wire-coating enamels, the silicones were found to be inherently deficient in adhesion. The free film of the alkyd resin had about twice the tensile strength of the silicone. However, when applied to the wire, the alkyd had ten times the flex life because the adhesion of the alkyd was so much better.

The catalysts used in curing have a marked effect on the adhesion of the resin to the metal surface. Triethanolamine produces best adhesion. Iron salts are intermediate and zinc salts are the worst.

The presence of residual OH groups on a polymer should improve its adhesion to aluminum by hydrogen bonding. By this reasoning SE-79 elastomer, containing residual OH groups, should improve the adhesion to metal.

A number of suggestions for improving adhesion by mechanical and other means includes roughening by sand blasting or grinding, phosphatizing, anodizing, and the use of Metlprep and Alumiprep which some people in the field feel are better than chromic acid cleaning to improve adhesion. The phosphatized surface has the disadvantage of an upper operating temperature limit of 800°F, at which temperature crystals of metallic phosphate tend to pop off.

Several materials have been suggested as primers. Linde's GS-1 sizing emulsion, which is a vinyl resin emulsion, has been suggested for use in very dilute concentrations - .05% to .1%. The primed object should be heated to 275°C for two minutes after drying at room temperature. Ethoxy silanes, particularly triethoxy silanes, in very dilute solutions have also been suggested for use as primers. Thin coats of epoxy resins or copolymers of epoxies with silicones have also been suggested as primers.

A method for testing the surface cleanliness of the metal by means of electrical conductivity has been proposed and might prove to be advantageous.

IV. EXPERIMENTAL WORK

A. Silicone Elastomers as Experimental Structural Adhesives

Silicone elastomers seemed particularly attractive as potential structural adhesives at the outset of this project because of their durability and capacity to absorb vibration and shock. The initial phase of the work with elastomers consisted of a screening of all of the commercially available silicone rubber-based adhesives in aluminum-to-aluminum bonds. X-6719A, the best adhesive from the room-temperature screening, also showed fairly good retention of shear strength at elevated temperatures. Furthermore, X-6719A was found to be more satisfactory as a structural adhesive for stainless steel than it was for aluminum. The difficulty of obtaining good adhesion between the silicone and the metal was recognized immediately. Exhaustive efforts to improve adhesion followed. Polymers were modified by chlorination and by the addition of fillers. Methods of modifying the surface of the metal were evaluated, including the use of primers. Since the problem of adhesion to the metal surface was not solved satisfactorily, the investigation of elastomers was terminated for the time being when it was shown that silicone resins developed higher bond strengths.

1. Screening of Silicone Elastomeric Adhesives

The compositions tested included:

Dow Corning X-6719A Bonding Adhesive
X-6708 " "
DC-110 " "
DC-112 " "
XC-270 Pressure-Sensitive Adhesive

Connecticut Hard Rubber 251 Bonding Adhesive
259 " "

General Electric SS-15 Bonding Adhesive
SS-64 " "
SE-100 Elastomer

CHR-261, CHR-259 and SS-15 are compounds of silicone elastomers, silicone oil, solvent thinner (xylene or toluene), a curing agent such as benzoyl peroxide, and reinforcing fillers such as finely divided zinc oxide and titanium dioxide. The remaining adhesives are thought to be similar, with the exception of XC-270 which is believed to be a resin polymer.

Throughout the entire test program with silicone elastomers, aluminum panels were cleaned by the chromic acid method suggested by Wright Field, and the shear strength tests were made by the standard method. For each particular compound, various cures were carried out either by following suppliers' instructions, or, in the absence of such instructions, by determining the desirable cure after observing the behavior of the elastomer when heated and tested. The most commonly used curing cycle for the elastomers was a half-hour press cure at 250°F, followed by an oven cure at 300°F for 12 and 16 hours. Most tests utilized a silane primer: either DC-796 or CHR-260. The experimental data for the screening of elastomeric adhesives is found in Tables 1 and 3.

X-6719A was most promising in room-temperature shear tests, with results averaging 700 to 800 psi when used undiluted or as a 50% solids solution. The best bonds observed for CHR-251 and CHR-259 were 308 and 415 psi, respectively (Panel Set Nos. 26 and 179). DC-110 and DC-112 gave shear strengths averaging slightly over 400 psi (Panel Set Nos. 325 and 326). The General Electric compounds, SS-64, SS-15 and SE-100, all gave shear strengths of between 200 and 300 psi (Panel Set Nos. 31, 78 and 324). A shear strength of only 110 psi was obtained with X-6708 (Panel Set No. 24). The pressure-sensitive adhesive, as expected, was not found to be useful as a structural adhesive.

The main point of failure of the strongest structural adhesives was in adhesion between the elastomer and the metal surface. In contrast, it is of interest to note that DC-110, DC-112 and SS-64 failed 100% cohesively, which may mean that they adhere better to aluminum than does X-6719A.

Bonds of X-6719A, prepared at the Connecticut Hard Rubber Company, were shear-tested at Wright Air Development Center at 500°F. (Table 20). A maximum shear strength of 275 psi, with an average of 200 psi, was found at that temperature.

A series of tests was made, using X-6719A to check the adhesion of silicone elastomers to steel rather than to aluminum. The steel panels were cleaned, using Cleaning Method C-5, and primed with a 10% solution of CHR-260; the X-6719A was applied, and the panels were set up in the jig. The adhesive was given a cure of 12 hours at 300°F, and the panels were tested at 70°F. An average shear strength of 865 psi was thus obtained with stainless steel test panels (Table 2, Panel Set Nos. 115 and 116). This average is about 100 psi greater than the average strength of aluminum-to-aluminum joints made with the same adhesive.

Shear tests were made on stainless steel panels bonded with X-6719A at certain elevated temperatures, 387° and 527°F, by the following method (prior to receiving the small, axially hinged electric furnace, later used). Panels were heated, after insertion in the tester jaws, by means of a hot-air gun which could develop a 650°F air-temperature at the nozzle. The bond area of the panel to be tested was heated directly by the air blast. The temperatures were measured, and the thermocouples were clamped to the panel at the bond area, both on the heated side (front) and the side away from the hot-air blast (back). The panel was heated to maximum temperature and held at that temperature for one minute before being tested. It is seen in Table 2 that this particular set of silicone bonds retained 57% of room-temperature strength at 387°F and 64% at 527°F when tested by the use of this method.

2. Modifying Silicone Elastomeric Adhesives

In order to substantiate the theory that better adhesion of elastomers to metal could be attained by the use of highly polar groups on the elastomer, samples of chlorinated silicone gums were tested. The initial results did indeed show a greater adherence of silicone elastomer to aluminum, but bonds of very low strength were obtained (Table 1). Mixtures of chlorinated silicone gum and X-6719A were prepared in different percentages and were tested both in conjunction with primer (Priming Method P-4) and without. Better results were attained without the use of primer. However, while bonds showing 100% cohesive rather than adhesive failure were obtained, the bond shear strengths were in the range of 285 to 300 psi, which is considerably lower than the original results obtained using X-6719A.

Fillers such as GS-Silica, Santocel-C and Aerosil silica were blended with X-6719A in an attempt to reinforce the bonds, but in every case the bond failure was 100% adhesive and the shear strength was lower than that with pure X-6719A (Table 1). Priming method P-1 was used. The cures for these blends ran from 16 to 24 hours at temperatures from 300° to 400°F. In no case was a shear strength of over 300 psi noted, however, while in some cases it ran as low as 10 psi.

3. The Effect of Primers on Adhesion

After the original investigation of commercial metal-to-metal adhesives and the subsequent realization that the main problem was one of forming a satisfactory adhesive-to-metal bond, the use of primers was thoroughly investigated. It had been

hoped that various priming agents used as an interface between the silicone and the metal would improve adhesion by bonding to the metal and in turn presenting a surface more similar chemically to the silicone structure. A number of such chemicals were available and it was therefore of interest to evaluate them as priming agents. These included orthosilicates (in Dow Corning 796); disilanes (in CHR-260; used in Priming Methods P-1 to P-8); sodium silicate, sodium methyl siliconate, silicon tetrachloride, titanium tetrachloride, methyl-trichlorosilane and dimethyl dichlorosilane.

An examination of Table 3 will reveal that the use of primed surfaces for bonding with silicone elastomeric adhesives has been extensively tested. X-6719A adhesive was used through the better part of the test program, and cleaning methods, primers and methods of priming, and time and type of curing were varied.

Dow Corning DC-796 primer compound and CHR-260 priming compound behaved equally well and, in general, were superior to other priming compounds. The highest shear strength obtained with a primed surface was 1025 psi (Panel Set No 68B). CHR-260 disilane primer was used. While the use of methyltrichlorosilane as a primer with this adhesive system gave a good bond strength (850 psi) on Panel Set #183, the bond failure here was 100% adhesive.

Sodium silicate and sodium methyl siliconate react with the aluminum metal surface in much the same manner as aluminum hydroxide, liberating hydrogen and forming a complex aluminum silicate or aluminum siliconate. The use of sodium methyl siliconate was of particular interest because in reacting with the aluminum surface it would be expected to produce a surface structure similar to that of the silicone adhesive. However, these materials did not produce good priming surfaces. Apparently they do not form a coherent layer on the aluminum, although they do react chemically with the surface. This is understandable because the hydrogen liberated during the reaction may well prevent the formation of an adherent film. Some additional experiments were carried out with sodium methyl siliconate, using a solution containing a hydrogen-accepting agent of the type used in plating solutions, but an adherent film did not form on the aluminum even under these conditions.

It was found that adhesion could be increased somewhat by the widely used method of applying thin, dilute coatings of the adhesive (X-6719A) to the metal surface and partially curing prior to application of the undiluted adhesive. The system

is similar to that used in present structural adhesives of the metal-bond type. The optimum procedure consisted in using one layer of 10% X-6719A, cured 10 minutes at 300°F as a priming coat. In Panel Set Nos. 163 and 164, shear strengths of 800 and 850 psi were attained with and without initial priming with CHR-26C. Bond failure in both cases was 70% adhesive, 30% cohesive. Further experiments, using multiple priming layers of dilute adhesive and curing the priming layer for longer periods did not improve the adhesion. These procedures, in fact, reduced the strength of the bonds.

Experience has shown that the silicone resins possess far better adhesion to the metal than do the rubbery adhesives. It was therefore thought that a thin layer of resin on the metal, previous to bonding with X-6719A, might greatly enhance adhesion. The resin primer layer might bond to the rubber by vulcanization through adjacent methyl groups of the resin and rubber, promoted by vulcanizing agent thought to be present in X-6719A. Three resins which had given strong bonds in shear tests were selected for trial as primers: SR-32, DC-996, and LC-994. Ten percent solutions of these resins in xylene were painted on aluminum panels which were then subjected to elevated temperatures for two hours to evaporate the solvent and partially cure the resin prior to the application of X-6719A adhesive. Samples were then cured in accordance with the method used for X-6719A. Three sets of control samples without resin primer layers were run simultaneously. Experimental conditions and the results of this investigation are shown in Table 3, Panel Set Nos. 298 to 306.

In each case the presence of resin primer layer considerably decreased the shear strength in comparison with the control sample. The poor results can perhaps be explained on the basis of incompatibility and chemical dissimilarity which exists between silicone resins and silicone rubbers. The silicone resins ordinarily react by condensation through OH groups, whereas silicone rubbers react by vulcanization through adjacent methyl groups. While it would be considered highly desirable to make full use of the excellent properties of shock-and-vibration-resistance of the silicone rubbers, it is felt at this time that the silicone rubbers do not possess the necessary internal stability to maintain a satisfactory bond at high temperatures.

4. The Effect on Adhesion of Anodizing the Aluminum Surface

In considering other means by which silicones could be made to adhere to aluminum surfaces, the possible use of the method by which aluminum is dyed was of interest. During the anodi-

zing of aluminum, a highly porous and absorptive layer of aluminum hydroxide is built up on the surface. To produce a hard, corrosion-resistant film, the anodized aluminum is sealed by treating with boiling water for about 30 minutes. During this sealing operation, the aluminum hydroxide film loses water to form a tightly adhering film of aluminum oxide monohydrate. Aluminum oxide is one of the hardest and most stable materials known. The anodizing and sealing process produces a hard, corrosion-resistant, mar-resistant surface on the relatively soft aluminum metal. To color aluminum, as is done with aluminum tumblers and plates, an organic dye is absorbed from aqueous solution into the porous aluminum hydroxide film before the sealing operation is carried out. The dye becomes sealed into the aluminum hydroxide coating during the sealing operation, and the net result is a strongly bonded dye coating.

It was thought that silicone materials could be sealed into the porous aluminum hydroxide surface in a similar manner to form a tightly bonded surface chemically similar to the silicone polymers being used as adhesives.

Aluminum panels were obtained which had been anodized by two different methods: electrical and chemical. These methods are described in more detail in Section V. An experimental program was carried out to evaluate potential silicone sealing agents and methods for bonding with X-6719A. The materials investigated included primarily low-molecular-weight silicone oils such as General Electric 81119 and 81392; heavier silicone oil such as GE SF-96; silicone emulsions such as GE SM-61 and Linde GS-1; "dimethyl tetramer" (octamethylcyclotetra-siloxane); diphenyl silanediol, and methyltrichlorosilane. The experimental technique usually involved immersion for 10 minutes in the hot (250°F) silicone material. In some techniques, the immersion in silicone was at room temperature, followed by sealing in boiling water for 30 minutes, as in the dye-sealing process. The experimental data and shear test results are presented in Table 4.

The most satisfactory adhesion with a silicone oil sealant was obtained with the use of GE 81119 oil on electrically anodized panels (Panel Set No. 151).

Panels, chemically anodized, were sealed with silicone oil by immersion for 10 minutes in hot, low-molecular-weight polydimethyl siloxane. Although this sealing took place in a non-aqueous medium, there was evidence that the aluminum hydroxide was undergoing the dehydration of the sealing operation, by virtue of the evolution of bubbles of water

vapor. Shear strengths of 465 and 490 psi were recorded, which, for all practical purposes, were identical to the control (470 psi).

Since absorption by a molecular film is concerned here, it was felt that the silicone oils represented too large a molecular size for proper absorption into the aluminum hydroxide film, and therefore a smaller silicone molecule of the same family was tested. The cyclic octamethyltetrasiloxane, known also as dimethyl tetramer, was chosen and tested, using electrically anodized aluminum panels with X-6719A as the bonding agent. Shear strengths of the bond were found to be 570 psi. This figure was raised to 725 psi when catalyzed tetramer was used and heat-treated to polymerize it on the surface, prior to application of X-6719A adhesive. However, the bond failure was 100% adhesive, and no evidence of increased adhesion was noted with the surface treatment.

Further experiments were carried out in attempts to seal silicone oils and resins to the aluminum hydroxide film from aqueous emulsions (Table 4). Separation of the emulsions during heating and low bond strengths were evidence of the dubious merits of this procedure.

A series of tests were conducted using CHR-260, methyltrichlorosilane, dimethyldichlorosilane and diphenylsilanediol as sealants on the anodized aluminum. The CHR-260 and the diphenylsilanediol were applied in solution and dried through solvent evaporation. The methyltrichlorosilane and dimethyldichlorosilane were applied to the panel by dipping and then immersing in water to hydrolyze the chlorine groups. While these primers did cause a decrease in the percentage of adhesive failure, the bond strengths were lower than the original control (Table 4).

These experiments indicate that the aluminum hydroxide surface produced by anodization does not prove to be a better bonding surface than that formed by the chromic acid method.

B. Evaluation of Silicone Resins and Silicone-Organic Copolymers

1. Experimental Cure Studies on Silicone Resin

The polymerization of the resins proceeds through a condensation reaction which produces water as a by-product; and, because of the irregular manner in which linkages are formed, polymerization is not completed in the first stage. A period

of exposure to high heats, preferably in the absence of solvent, is necessary to complete the polymerization. This last operation is called the curing. The period of curing differs for various resins, and the suppliers generally indicate optimum cure times in their technical information. The resins are being used under this contract, however, for purposes other than those intended by the manufacturers. It was discovered in early experiments that one of the chief faults in the processing of silicone resins is insufficient curing. Many such resins go through a brittle stage during the curing before reaching the ultimate flexibility necessary in structural adhesives.

A survey of the manufacturers' literature revealed that the curing requirements of silicone resins cover a wide range of time and temperature; many of the resins require cures at 430°F and many of them require cures for long periods of time in order to develop optimum properties. It was deemed necessary to determine the optimum cure time and temperature necessary to develop the strength, firmness and flexibility desirable in a structural adhesive bond.

Two experiments were carried out (Tables 5 and 6), the first covering short cures at temperatures of 300° to 450°F, the second long cures at 480°F to obtain information as to which resins would be sufficiently flexible for structural adhesives and what cure times and temperatures would be necessary to develop strength.

Examination of the cured resin samples showed that the silicone resins, when cured adequately, possess properties desired in high-temperature structural adhesive materials. Three primary requirements of potential structural adhesives are high strength, flexibility, and resistance to high temperatures. The resins which show high strength and also satisfactory flexibility after the various cure cycles are SR-17, SR-28, SR-32, GE-81390, GE-81397, LC-935, LC-993, DC-994, DC-996, X-61, Y-1043 and Y-1044.

Several observations were made regarding the curing requirements and properties of the various resins. Wide latitude in the necessary curing times was noted. Several of the resins are very fast-curing. They appeared to have reached their optimum cure after only one hour at 300°F. These include SR-80, GE-81369, DC-2103, and XR-261 and Linde X-14C. They have the disadvantage, however, of being very hard and brittle, a characteristic which presumably would reduce the vibration-resistance of a structural adhesive. The resins requiring the longest cures are the low-numbered GE resins,

SR-17, SR-28, and SR-32, and the Dow Corning 900 series, particularly 935 and 996. Experimental observations verified the fact that the low-numbered General Electric resins, SR-28, and SR-32, are definitely flexible, whereas the higher numbered ones, SR-53, SR-61, SR-80 and SR-82, become increasingly less flexible.

The experimental cure study of the copolymers reported in Table 7 was conducted in a manner similar to that carried out with the unmodified silicones. Most of the copolymers appeared to be cured after only two hours at 480°F. The exceptions were one silicone-alkyd and the silicone-epoxy, which were cured after four hours. One material, clear silicone 160-25-D, remained semifluid and very tacky even after 36 hours at 480°F.

Observations made at room temperature after six hours at 480°F showed two of the copolymers, Silicone-Alkyd Oil Modified 160-30-D and Silicone-Epoxy X-2720, resins which had high shear strengths, to be somewhat flexible after curing. While this property would probably contribute to good vibration-resistance in a structural adhesive, harder, more brittle materials would not necessarily be unacceptable. Three other silicone-alkyds, X-2608, RS-556 and RS-513, which had high shear strengths, were found to be hard and brittle after curing. The silicone-phenolic and a modified silicone of lower shear strength were found to have good flexibility.

It was observed that these copolymers were soft at 480°F, as were the unmodified silicone resins. It was therefore anticipated that the addition of suitable fillers or catalysts would be required to improve the high-temperature shear strength. A part of this program has been carried out and is discussed in Part D.

2. Screening of Silicone Resins

All commercially available silicone resins were tested for their shear strengths in structural adhesive bonds. Many silicone resins were obtained from Dow Corning Corporation, General Electric Company and Linde Air Products Company. In addition, silicone-styrene copolymers were obtained from Linde Air Products Company. Silicone-epoxy, silicone-alkyd and silicone-phenolic copolymers were received from Midland Industrial Finishes Company. Such copolymers have been reported to adhere better to metal than do pure silicones.

In the earliest work with the resins, short-time or low-temperature curing cycles were used. The experimental details

and room-temperature shear test results are reported in Panel Sets numbered below 250 in Table 8.

Shear strengths of over 900 psi were obtained with two hour cures at 500°F (SR-32 and DC-993 resins). A maximum shear strength of 685 psi was achieved with a 16-hour oven cure at 300°F (DC-803 resin). A maximum strength of 308 psi was obtained (DC-802 resin) in bonds cured in a press for one hour at 300°F without a post-mold cure.

A good standard bonding technique was subsequently developed through experimentation. The resin was painted on the panels from a solvent solution. The panels were held at 150°F for about 1½ hours to evaporate the solvent. The resin on the separate panels was then partially cured for ½ or 1 hour at 300°F to prevent it from running out of the glue line during curing. The bonded samples were held in the press at contact pressure at 300°F for ½ hour to "join" the panels. Additional pressure tended only to force the resin out of the glue line.

A new resin-evaluation program through room-temperature shear tests was set up, utilizing the new techniques. As a result of the cure studies reported above, a standard cure of 16 hours at 480°F was selected so as to be certain to cover the cure requirements of even the slowest resins. The shear strength values improved greatly with the use of the new techniques.

The results of the evaluation are reported in Table 8 (panel sets numbered above 250) for the commercial silicone resins and in Table 9 for the silicone-alkyd, silicone-phenolic, silicone-epoxy and silicone-styrene copolymers. DC-996 resin had an average shear strength of over 1900 psi as compared to 50, obtained with the previous techniques. Many resins showed bond strengths over 1300 psi.

Two silicone-alkyds and a silicone-epoxy (Panel Set Nos. 338, 347 and 348, Table 9) showed average shear strengths of nearly 1600 psi. Other silicone-alkyds and the vinyl silicone-styrene copolymers also gave very good bond strength, over 1400 psi. The silicone-phenolic copolymer and two of the modified silicones were not quite as satisfactory, with bond strengths under 800 psi. While these bond strengths are not markedly better than those obtained with unmodified silicone resins, they are equally good and certainly warrant a thorough investigation.

A point which may well be brought up at this time although it is more thoroughly discussed elsewhere in this report, is the fact that the bond shear strength given is actually the shear strength of the resin-to-metal bond. Since most of the experimental bond failures were adhesive, there is no way of knowing what the ultimate shear strength of the resins itself is until 100% cohesive failure is obtained.

3. High-Temperature Shear Tests on Silicone Resins

An experiment was carried out to determine the relationship of shear strength to temperature of test for LC-996 resin, the best bonding material at that time. The test panels were given the standard cure, and shear strengths were determined at room temperature, 100°, 125°, 150°, 175°, 200°, and 250°F. The shear strengths and heat-conditioning data are recorded in Table 11, and a curve has been plotted of psi shear strength versus temperature (Figure 1). It can be seen from the graph that shear strength falls rapidly up to 200°F, and then levels off at about 100 psi for this particular resin.

To determine the potential effectiveness of the silicone resins as structural adhesives for high-temperature service, a final screening program was carried out. All of the commercially available resins were used to prepare structural adhesive bonds of aluminum to aluminum, using the new techniques and 480°F cures. In most cases, four bonds of a resin were prepared and cured simultaneously. Two were shear-tested at 70°, one at 300° and one at 500°F.

The survey shows (Table 10) that many of the resins perform considerably better at high temperatures than did LC-996. A term was coined to describe the effect of high temperature on shear strength of the resin bonds. "Thermal efficiency" refers to the percent of the room-temperature strength which a resin has at high temperature. A resin with a moderate shear strength which retains a high percentage of its strength at 300° and 500°F is considered definitely more promising than one with very high initial shear strength which loses most of its strength at high temperature. The resins with "thermal efficiencies" of at least 60% at 300° and 35% at 500°F are: GE-81397, SR-82, LC-40-C, LC-804, DC-2103, DC-2104, DC-2105, DC-2106, XR-100 and XR-544.

The effect of test temperature on the shear strength of each resin was plotted. The curves for all of the Dow Corning resins are shown in Figures 3 through 8, those for General Electric resins are shown in Figures 9 and 10, and those for Linde resins may be found in Figure 11.

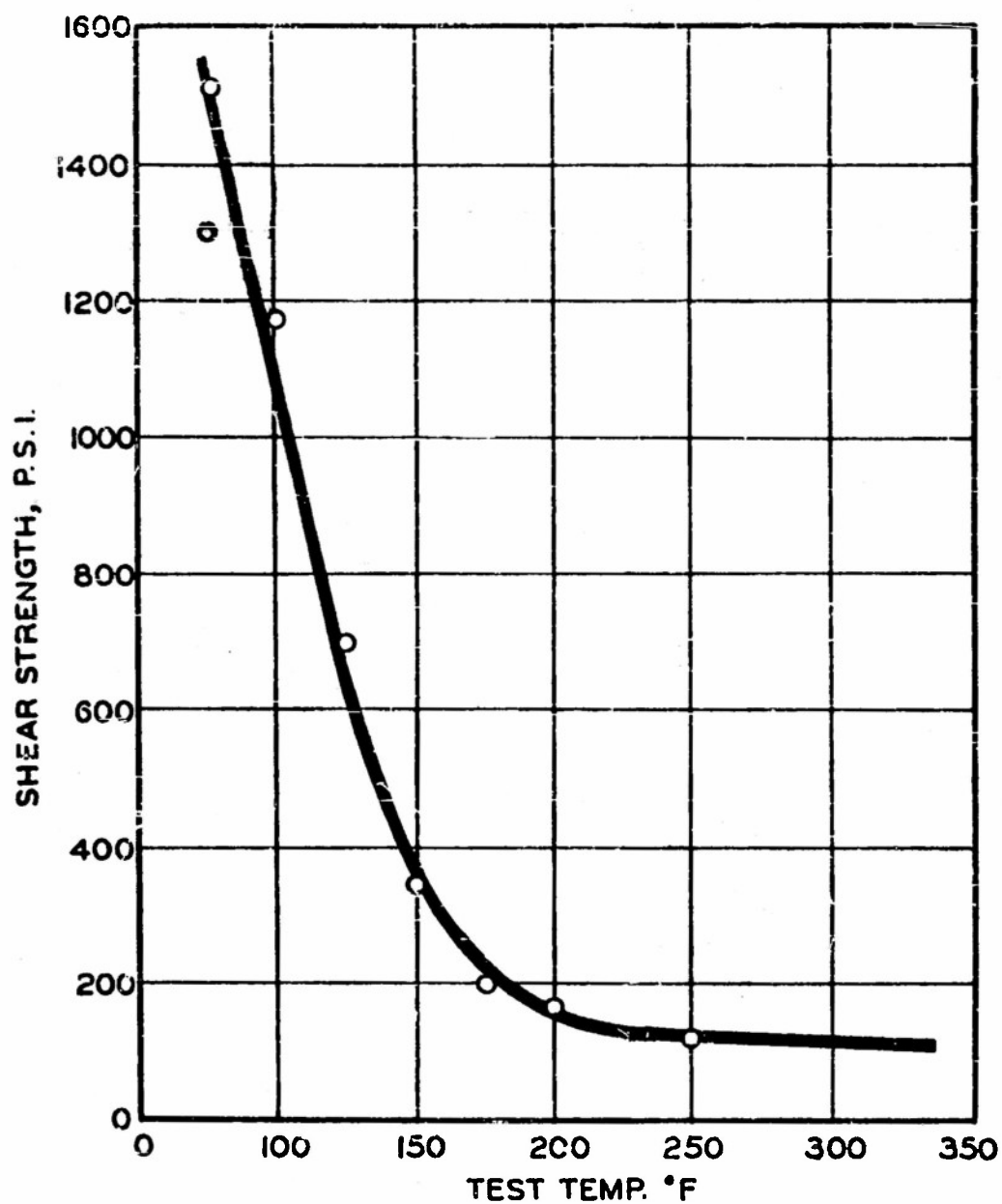


FIG. 1 THE EFFECT OF TEMPERATURE ON THE SHEAR STRENGTH OF DC-996 SILICONE RESIN.

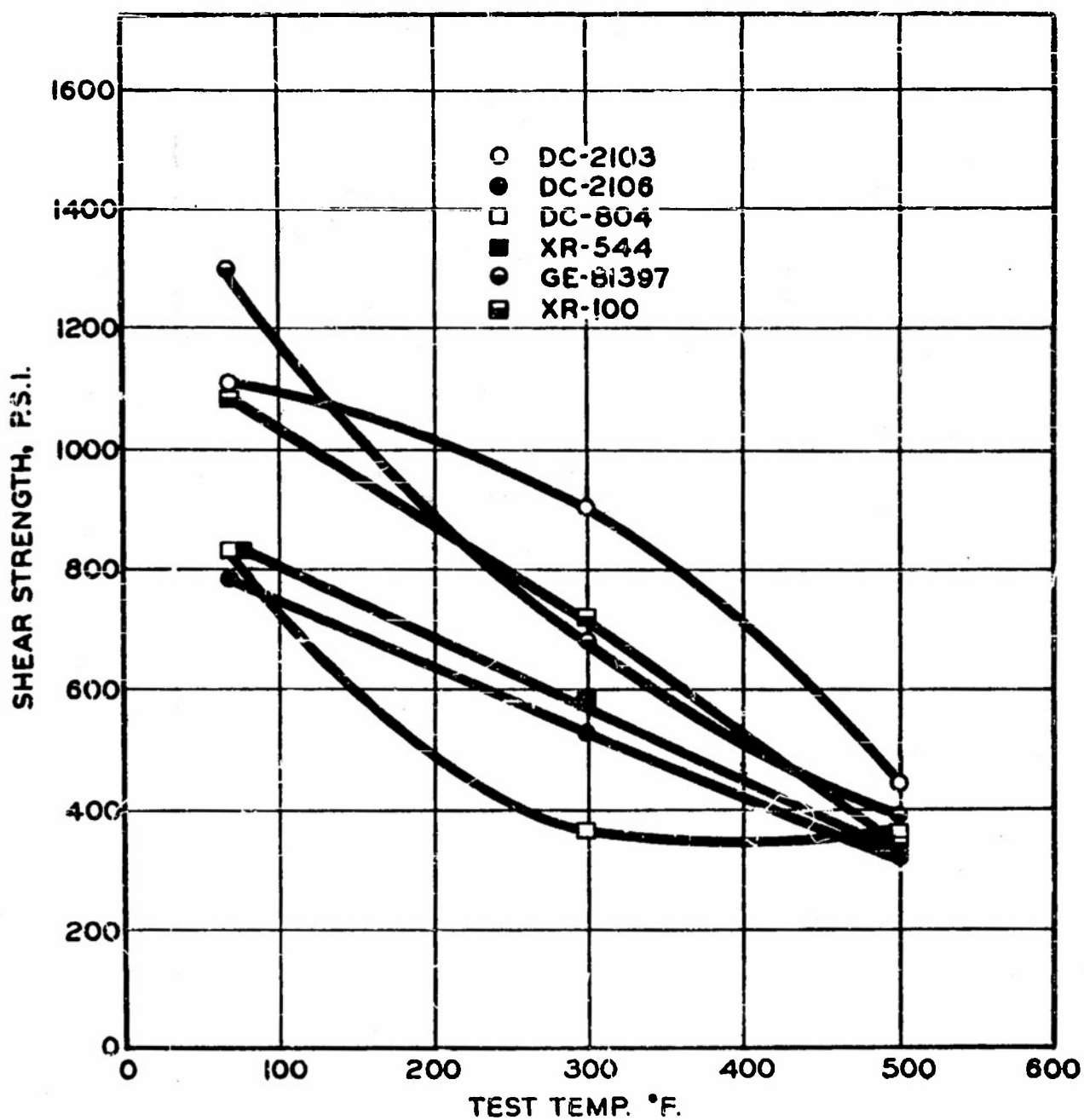


FIG.2 SHEAR STRENGTH VS. TEMPERATURE OF SILICONE RESINS SHOWING MIN. THERMOPLASTICITY.

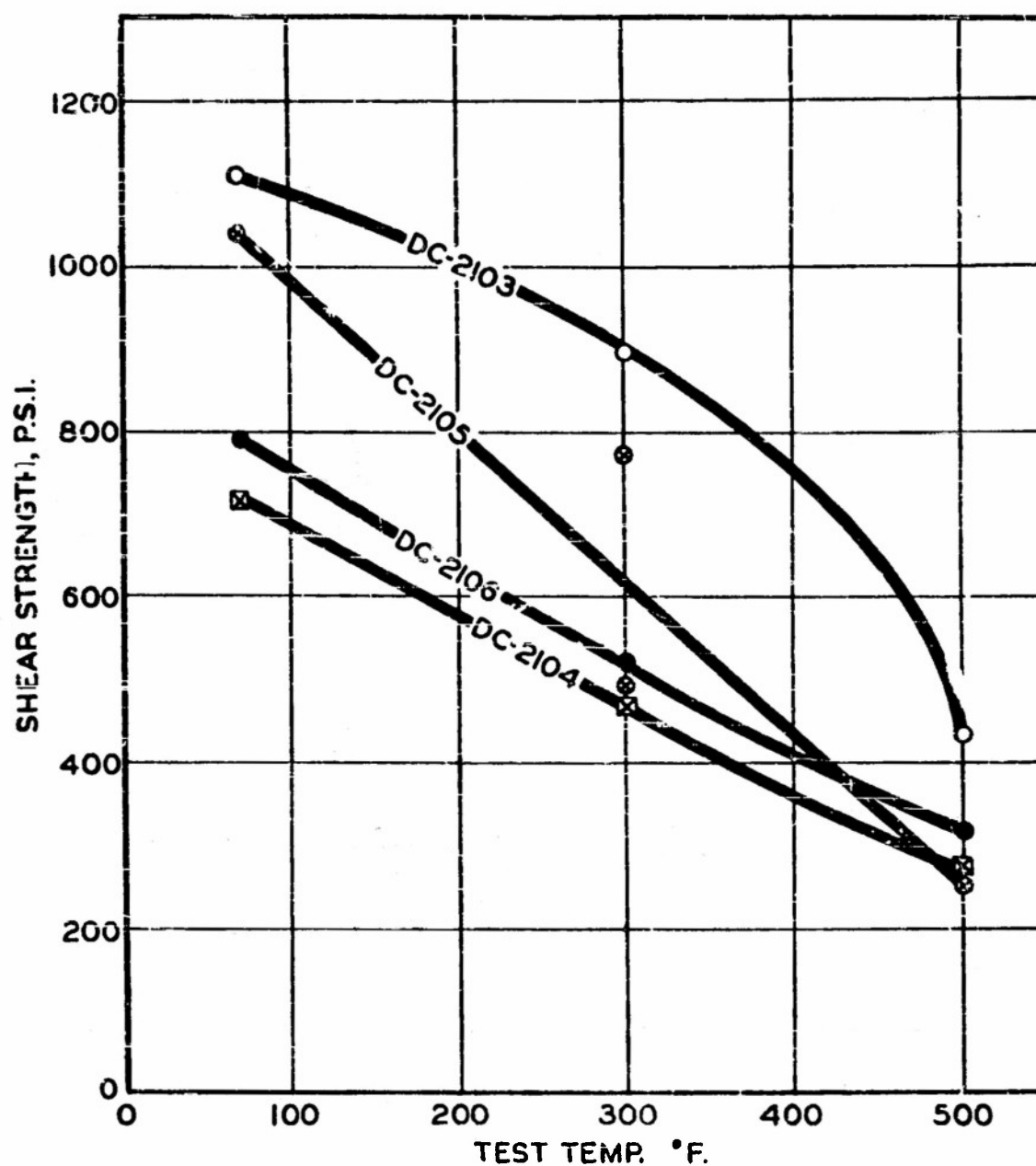


FIG. 3 SHEAR STRENGTH VS. TEMPERATURE OF SILICONE RESINS [DOW CORNING BONDING RESINS].

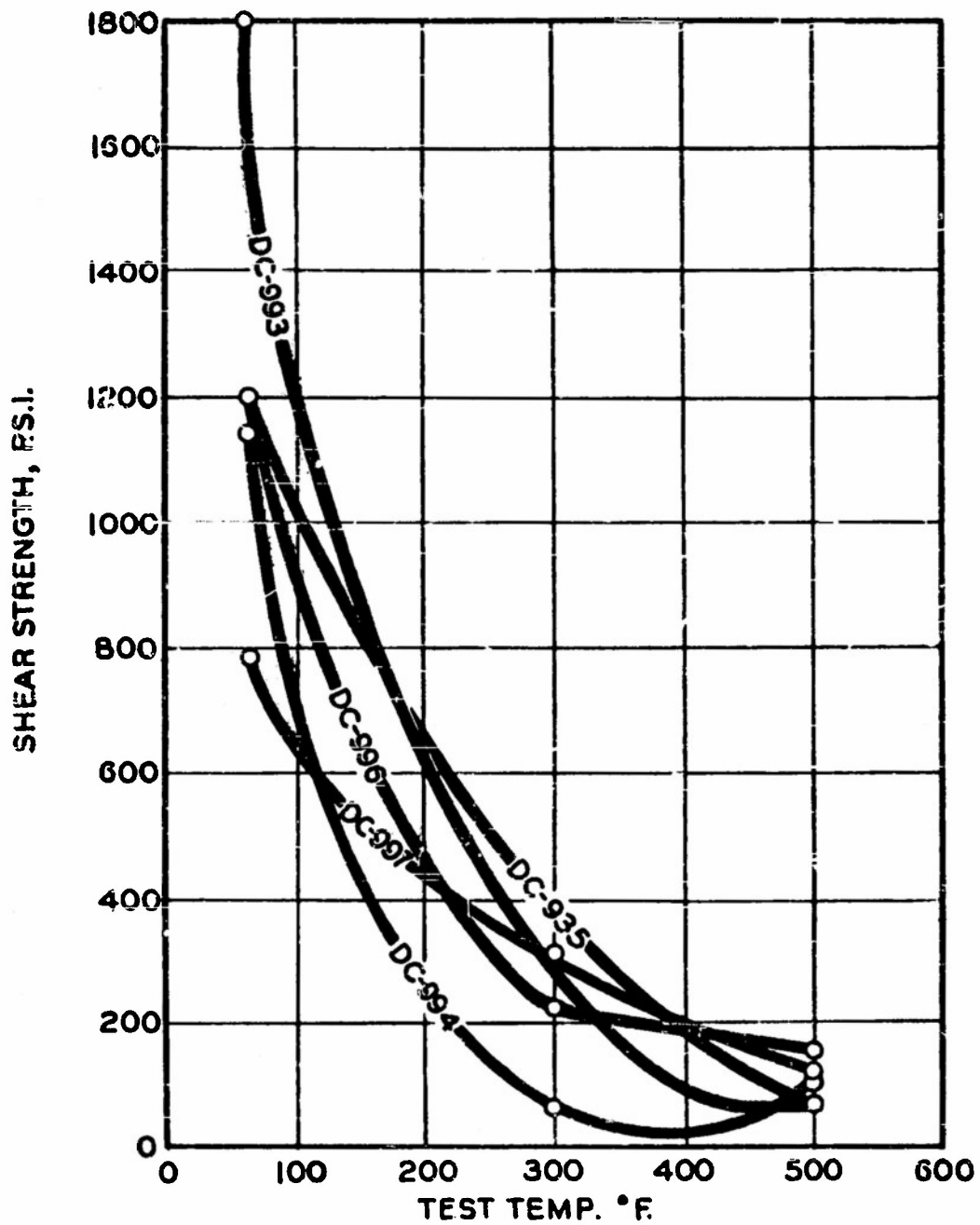


FIG. 4 SHEAR STRENGTH VS. TEMPERATURE OF SILICONE RESINS [DOW CORNING ELECTRICAL INSULATING VARNISHES].

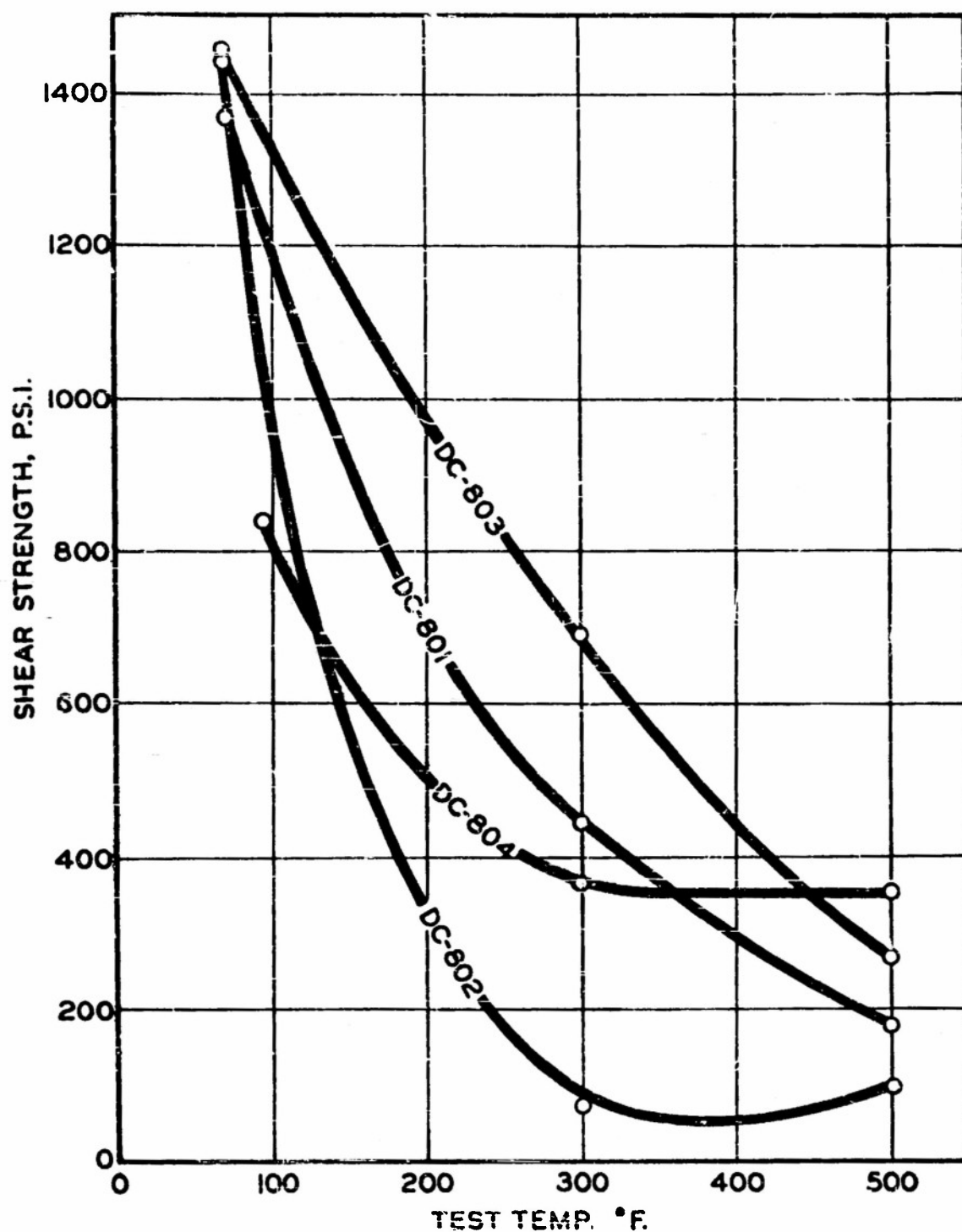


FIG. 5 SHEAR STRENGTH VS. TEMPERATURE OF SILICONE RESINS [DOW CORNING PROTECTIVE COATINGS].

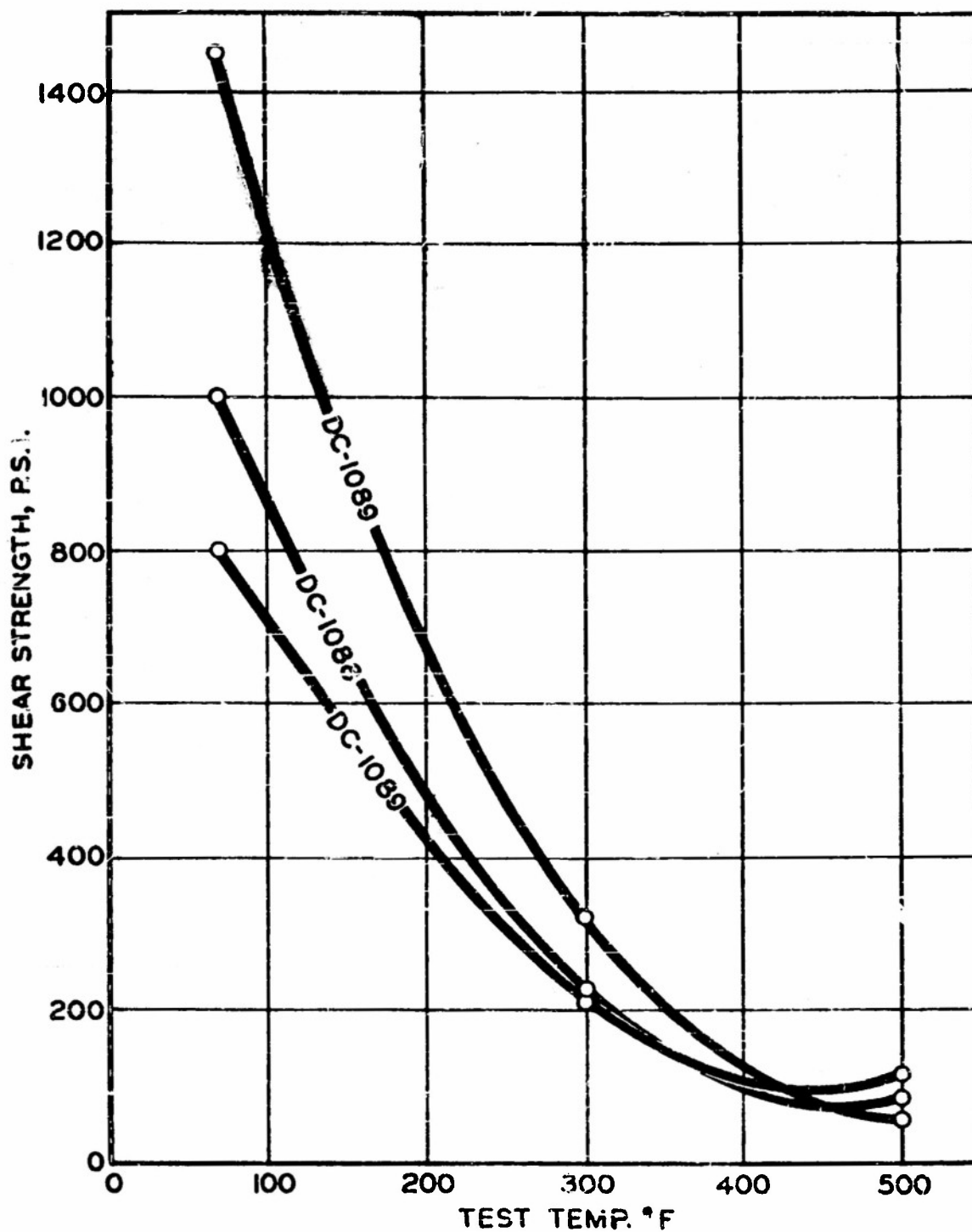


FIG. 6 SHEAR STRENGTH VS. TEMPERATURE
OF SILICONE RESINS [DOW CORNING
WIRE INSULATING VARNISHES].

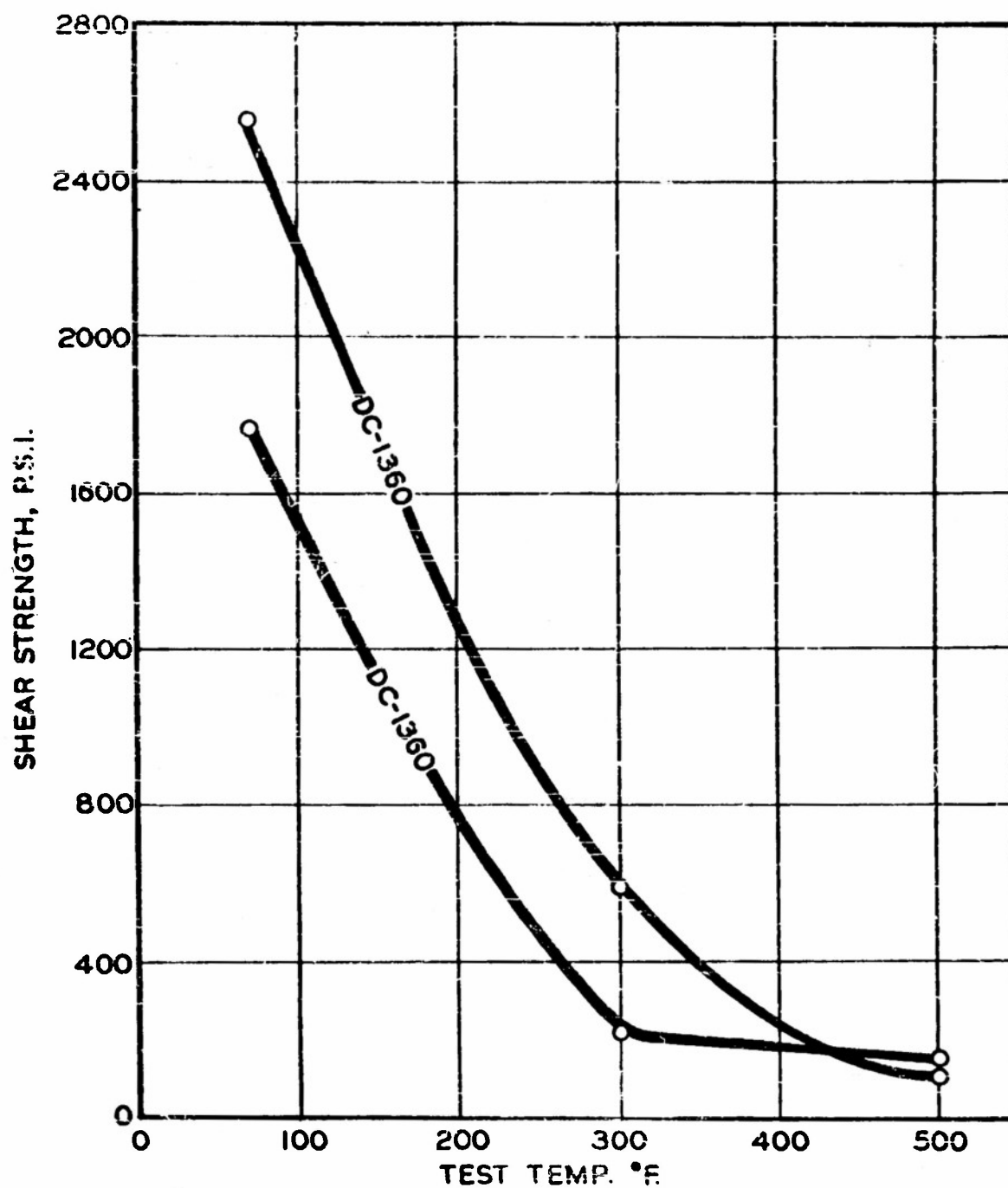


FIG. 7 SHEAR STRENGTH VS. TEMPERATURE OF SILICONE RESINS [DOW CORNING WIRE ENAMEL].

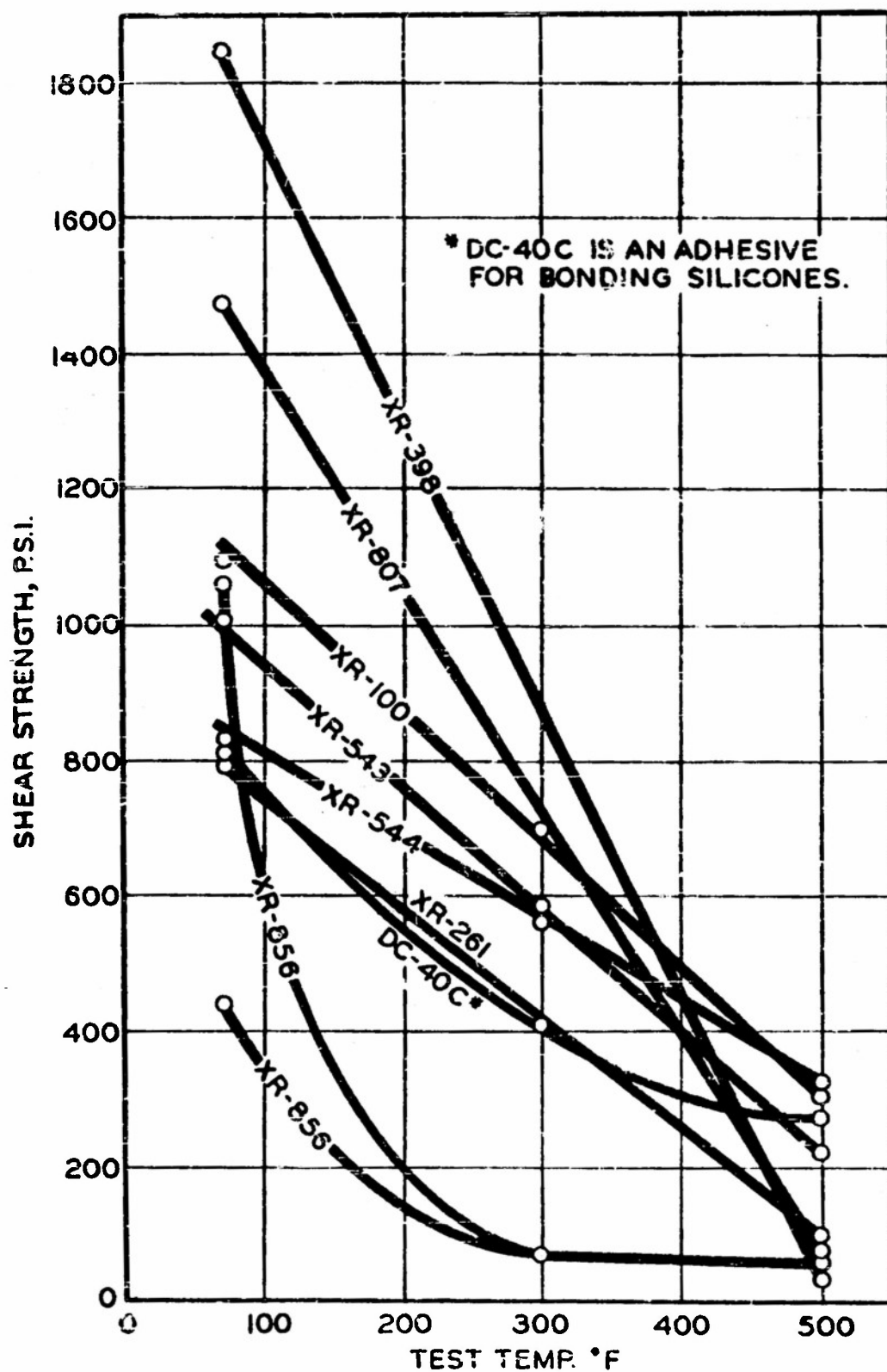


FIG. 8 SHEAR STRENGTH VS. TEMPERATURE OF SILICONE RESINS [DOW CORNING EXPERIMENTAL RESINS].

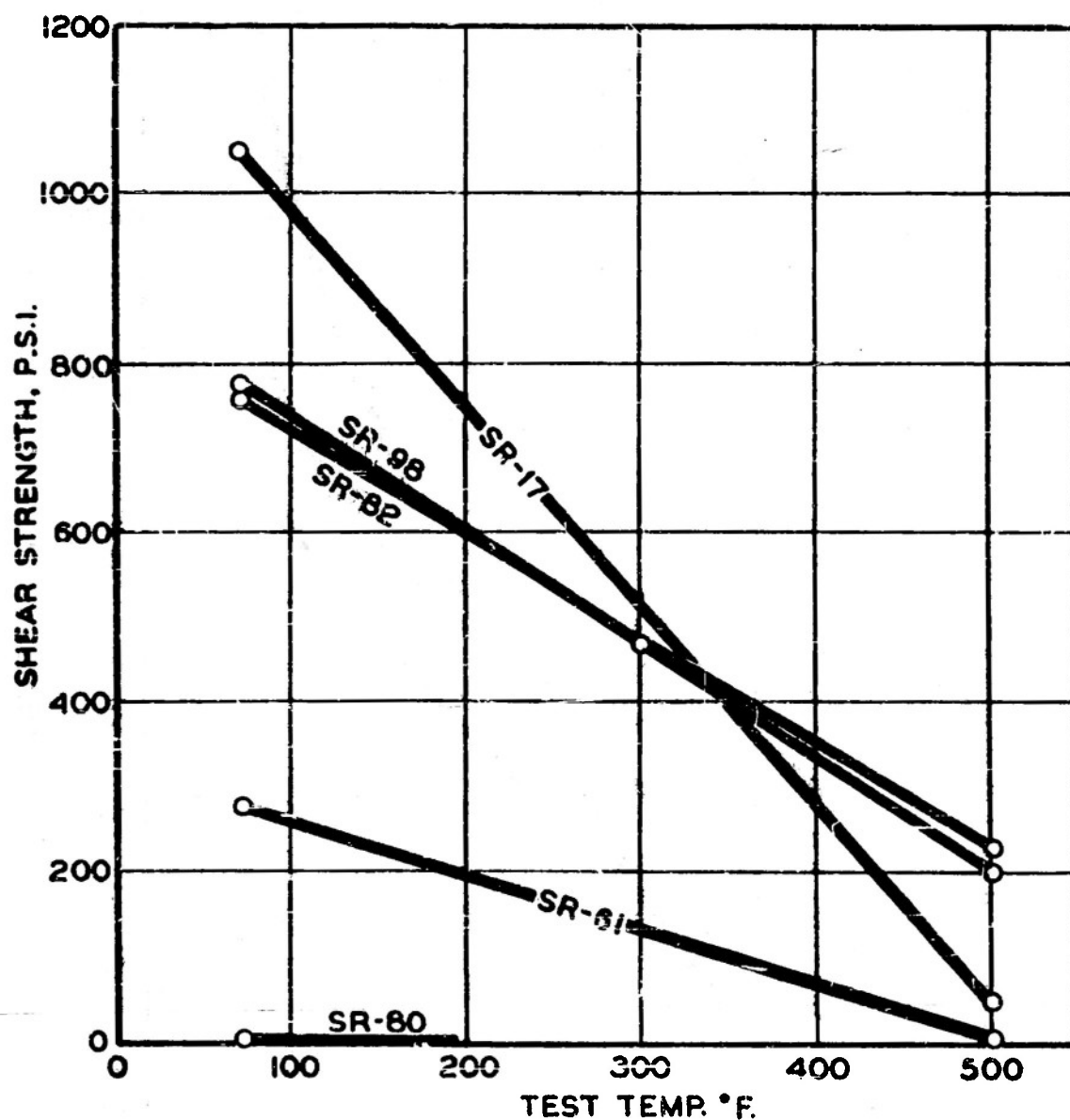


FIG.9 SHEAR STRENGTH VS. TEMPERATURE OF SILICONE RESINS [GENERAL ELECTRIC COMMERCIAL RESINS].

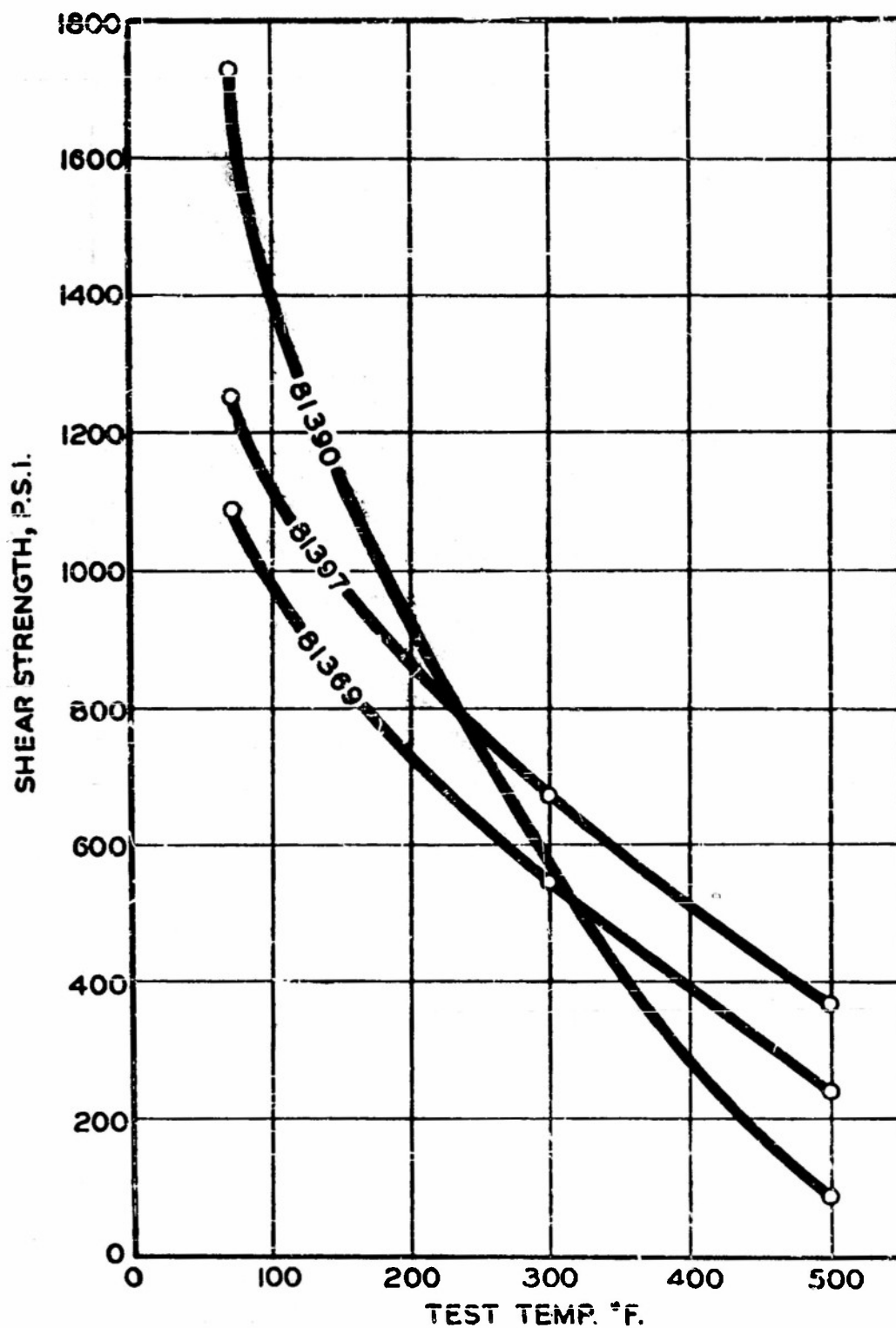


FIG.10 SHEAR STRENGTH VS. TEMPERATURE OF SILICONE RESINS [GENERAL ELECTRIC EXPERIMENTAL RESINS].

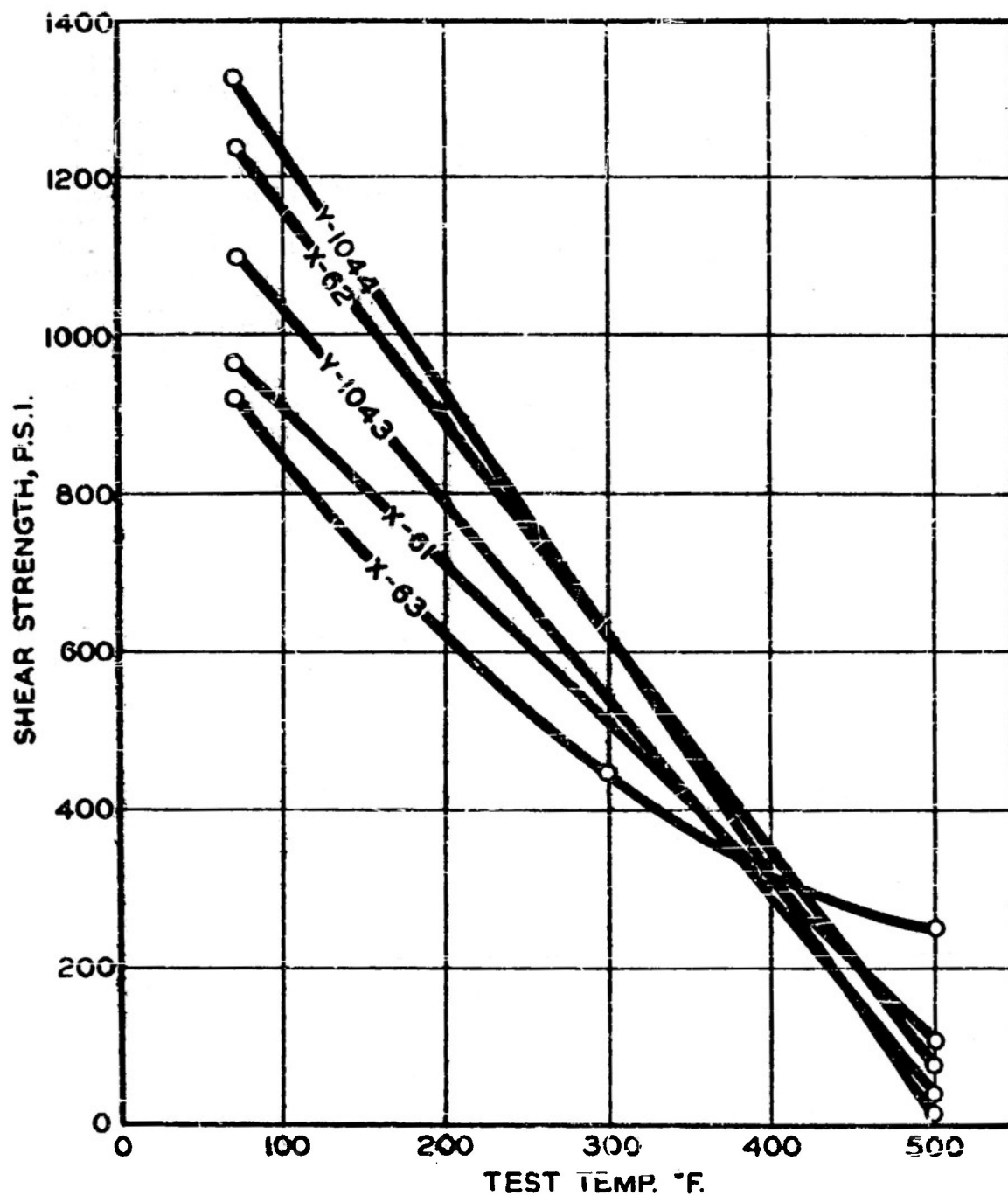


FIG. II SHEAR STRENGTH VS. TEMPERATURE OF SILICONE RESINS [LINDE SILICONE RESINS].

While the curves show the weakening of bonds due to thermo-plasticity, they also show very clearly which of the resins possess inherently the internal characteristics for strength at high temperatures. These are DC-2103, DC-2106, DC-804, XR-100, XR-544 and GE-81397. The curves for these resins have been duplicated and plotted together in Figure 2. All six of these possess shear strengths of at least 350 psi at 500°F. In addition to these, DC-803, DC-2105 and XR-544 showed promise for high-temperature use. These had high shear strengths (over 600 psi) at 300°F. The best group of resins for high-temperature use appear to be the Dow Corning 2100 and 800 series, bonding and protective coating resins, plotted in Figures 3 and 5. High-temperature shear tests were not completed on the copolymers from Midland Industrial Finishes Company.

4. Summary of Results of the Screening of Resins

Arbitrary standards of good performance were made to separate those resins showing the most promise for further experiment from the rest of the resins. A shear strength of at least 1300 psi was the criterion at room temperature. Resins with at least 600 psi at 300°F, or 350 psi at 500°F, were considered promising high-temperature resins.

The following resins are the best, based on these criteria.

<u>Room temperature</u>		<u>High Temperature</u>	
Dow Corning	801	Dow Corning	803
	802		804
	803		2103
	993		2105
	994		2106
	996		XR-100
	1089		XR-543
	1360 silicone-alkyd		XR-544
	2103	Gen. Elec.	81397
	XR-398		
	807		
Gen. Elec.	SR-32		
	81390		
Linde	Y-1043 silicone-styrene		
	Y-1044 " "		
	X-62		
Midland	X-2608 silicone-alkyd		
	RS-513 " "		
	RS-556 " "		
	160-30-D " "		
	X-2720 silicone-epoxy		
	160-29-H		

The resins for the studies on modification of resins with fillers and catalysts, reported in Part D to follow, were selected from this list. The future experimental work will be concentrated on, but not restricted to, these resins. It is hoped that a means for modifying the resins which exhibit good room-temperature strength will be found which will impart strength at high temperatures. An additional investigation of catalysts, fillers and chelates is planned.

5. Primers and Surface Preparation

The problem of improving the resin-to-metal bond remains a constant difficulty. The bond failures continue to be almost exclusively 100% adhesive failures, and the ultimate potential strength of the resins is therefore not being effectively utilized. Efforts to overcome this difficulty have taken many directions. Of primary interest, was treatment of the surface, prior to application of the resin. A priming material or procedure which would condition the surface or any material which would show greater adherence than silicone resins and still be compatible with them, would promote a bond of higher shear strength than is now being obtained.

a. Cleaning

Since the outset of this project, the aluminum test panels have been cleaned almost exclusively in accordance with the chromic acid method suggested by Wright Field (Method C-1). A brief test, using a commercial cleaning compound called "Alumiprep" (Method C-3) which is intended for the preparation of aluminum for painting, was made to determine the effect of pretreatment of aluminum panels on shear strengths, if any. The results of the test indicated that Alumiprep is as effective as the chromic acid cleaning method. It is also a simple method to use. The test results are on the last page of Table 8.

b. Priming

A further extension of surface preparation has involved the use of primers. The idea of a primary coat of silica-type compound has been followed from the beginning of the project. The use of CHR-260 primer (Method P-4) proved to have little, if any, effect on shear strengths of silicone resin bonds (Table 8). Its use was therefore abandoned.

c. Anodizing

A few of the best silicone resins and copolymers from the screening program were selected for determining the effect of anodizing the aluminum surface on the shear strength of the bonds. The resins and copolymers were applied directly to electrically anodized surfaces in an attempt to utilize chemical bonding by a condensation reaction between the hydroxyl groups in the anodic coating and the reactive groups contained in the resin. It is believed that the use of unsealed, rather than sealed, anodized surfaces is more likely to bring about the desired chemical bonding with the resin. The theory behind the use of anodized aluminum panels is discussed in more detail in Part A, preceding this section. The shear test results are reported in Table 12.

The only result which was significant was a 25% to 30% increase in bond strength with one of the silicone-alkyds (Panel Set No. 355) above that obtained with acid-cleaned, primed clad aluminum. Perhaps the greater shear value can be accounted for on the basis of improved adhesion, attributable to the type of chemical bonding mentioned above. Since the other resins and copolymers tested on anodized aluminum yielded shear test results lower than those obtained with the standard chromic acid surface-cleaning, the evaluation of anodizing was terminated for the time being.

C. Blending Resins and Rubbers

When rubbery structural adhesives are subjected to shearing stresses, the greatest amount of stress is concentrated at the edges of the bonded area because of the elasticity of the adhesive. With this type of uneven stress distribution, actual peeling of the adhesive results. While it was known from previous experience with silicone materials that, in general, silicone resins and silicone rubbers have little compatibility with each other, it was believed that if a compatible system could be obtained, the addition of silicone resin to the elastomer would increase the stiffness of the adhesive and thereby reduce bond failure due to peeling. The presence of the resin would also be expected to improve the adhesion to the metal, due to chemical bonding between residual OH groups on the resin and the water absorbed on the surface of aluminum.

A preliminary study of compatibility was made in which various silicone resins were used, together with three silicone elastomers: SE-76, an all-methyl polymer; polydiphenylsiloxane of low molecular weight, synthesized in this laboratory; and X-6719A, a compounded adhesive which is presumed to be predominantly a methyl elastomer. Ten percent solutions (in xylene) of each elastomer were mixed in test tubes with solutions of each resin (in xylene or toluene). While it is recognized that compatibility of dilute solutions of two materials does not guarantee compatibility of solvent-free mixtures of the materials, this experiment was designed to eliminate from further consideration those combinations which are totally incompatible, even in dilute solutions. All of the resins were found to be compatible with the low-molecular-weight polydiphenylsiloxane, thereby indicating that silicone resins are more likely to be compatible with phenyl than with methyl elastomers. SR-80 was the only resin tested which was compatible with the SE-76 and the X-6719A (see Table 13).

Mixtures of SR-80 and X-6719A were prepared in various proportions and applied to aluminum panels as bonding materials. The samples were cured in the same manner as was X-6719A, alone, except that the curing time was considerably longer, for the benefit of the resin. However, the panels bonded with the mixtures had no strength at all (see Table 14).

Aluminum panels were also bonded with mixtures of X-6719A and resins which were found to be incompatible with it (in this case, SR-32 and LC-993). The mixtures were prepared by milling the solvent-free resin into the elastomer. Aluminum panels to which the mixtures were applied as bonds were cured

by use of the methods used for the elastomer. The shear strengths proved to be considerably lower, however, than those obtained with either the pure resins or pure X-6719A (see Table 14).

Failure, in all cases, was entirely adhesive. The shear strengths of bonds obtained from mixtures of X-6719A and solvent solutions of other resins (DC-935, DC-2104 and SR-82) were also negligible (see Table 14). It was concluded that mixtures of silicone resins with silicone rubbers offered little promise for use as bonding materials.

D. Compounding Silicone Resins and Copolymers to Make Structural Adhesives

1. Introduction

The screening of silicone resins and copolymers reported above has shown that many silicone resins and silicone-organic copolymers have the potentialities for being good structural adhesives at ordinary temperatures. The screening shear tests at 300° and 500°F, however, have disclosed that shear strength diminished rapidly as the testing temperature was increased. Observations revealed that these bond failures are caused almost entirely by thermoplasticity.

It has been found in the last few years that with many polymers, particularly molding compounds and epoxide-phenolic adhesives, the addition of suitable fillers stiffens and greatly increases the high-temperature strength of the polymers.

Thermoplasticity of siloxane resin polymers can perhaps be accounted for on the basis of insufficient polymerization, i.e. the presence of too large a proportion of "too short" chains which are not cross-linked sufficiently with other chains. In practical applications, this means that they are not thoroughly cured. The chief means of increasing the extent of cure are: a) to increase the time and temperature of cure, and b) to add catalysts of polymerization to the resin prior to curing. It would be impractical to increase the time of cure (16 hours @ 480°F was used in the screening). It was thought, however, that the addition of the right catalyst might markedly increase the ultimate extent of polymerization by cross-linking of the resin chains, thus reducing the thermoplasticity observed. It is also likely that required cure times can be reduced by the use of catalysts. This possibility has not yet been investigated.

2. The Effect of Fillers on Shear Strength and Thermoplasticity

The fillers selected for evaluation were aluminum dust, mica dust, Santocel, Celite, titanium dioxide, and Agerite Alba. Aluminum dust has been shown by Shell Chemical Company to improve vastly the high-temperature strength of epoxide-phenolic resins. Celite and Santocel have been found to be excellent fillers for silicone molding resins, yielding molded products of excellent high-temperature strength. Both Santocel and titanium dioxide have been found to be excellent fillers for silicone elastomers. Mica dust had been recommended by other people in the field as a potential means of increasing

high-temperature strength of silicone resins. Agerite Alba was included as an antioxidant-type filler. Each of these was therefore considered worthy of evaluation for structural-adhesive purposes.

The first of two experiments with fillers was designed to determine which of three grades of mica available would be the most effective filler. DC-996 resin, which had given the greatest shear strength (70°F) to date, was chosen as the base resin. Proportions varying from 5 to 50 parts of each type of mica were added to 100 parts of resin, and aluminum test panels were bonded from the mixtures.

Room-temperature shear tests showed that the Ground White Muscovite Mica (Mineralite's) gave the highest shear strengths of the three types used. The two smallest proportions, 5 and 20 parts, gave the best shear strengths, but only equal to those of the control samples. It is readily observed (Table 15) that the presence of mica filler reduces the cohesive strength of the resin at 70°F. Cohesive failures result in all mica-filled samples, whereas adhesive failures result in all the unfilled control samples.

The major study of fillers consisted in determining the value of the various fillers on the high-temperature shear strength of selected silicone resins. The above-mentioned fillers were added in proportions varying from 10 to 50 parts to DC-804, 996, and 2105 pure silicone resins and to X-2608 silicone alkyd copolymer. DC-996 and X-2608 were selected because they had very good 70°F shear strength but poor high-temperature shear strength. DC-804 and 2105 were selected because they showed fairly good thermal efficiency (retention of room-temperature shear strength when tested at high temperatures.) The shear strengths of bonded aluminum test panels (bonded with the filled resins) were determined at 70°, 300° and 500°F. The results are recorded in Table 16 and presented graphically in Figures 12 through 17. The following observations can be made from the data. Of the four resins, DC-2105 seems to have the best strength at 300°F, whereas DC-804 is the strongest at 500°F. DC-804, an all-methyl silicone polymer, seems to be the most improved by the addition of fillers. Aluminum dust, mica dust, Santocel and Celite all improved its strength at 300°F, though its strength at 500°F is not significantly improved by any of the fillers. The shear strength of DC-2105 resin at 500°F is improved somewhat by aluminum dust. DC-996, the strongest of the three pure silicones at room temperature, has the poorest high-temperature strength of the three. Small amounts of Santocel, Celite, Agerite Alba, and titanium dioxide improved its room-temperature shear strength somewhat. Large amounts (50 parts) of mica dust, Celite and titanium dioxide improved its 300°F strength somewhat.

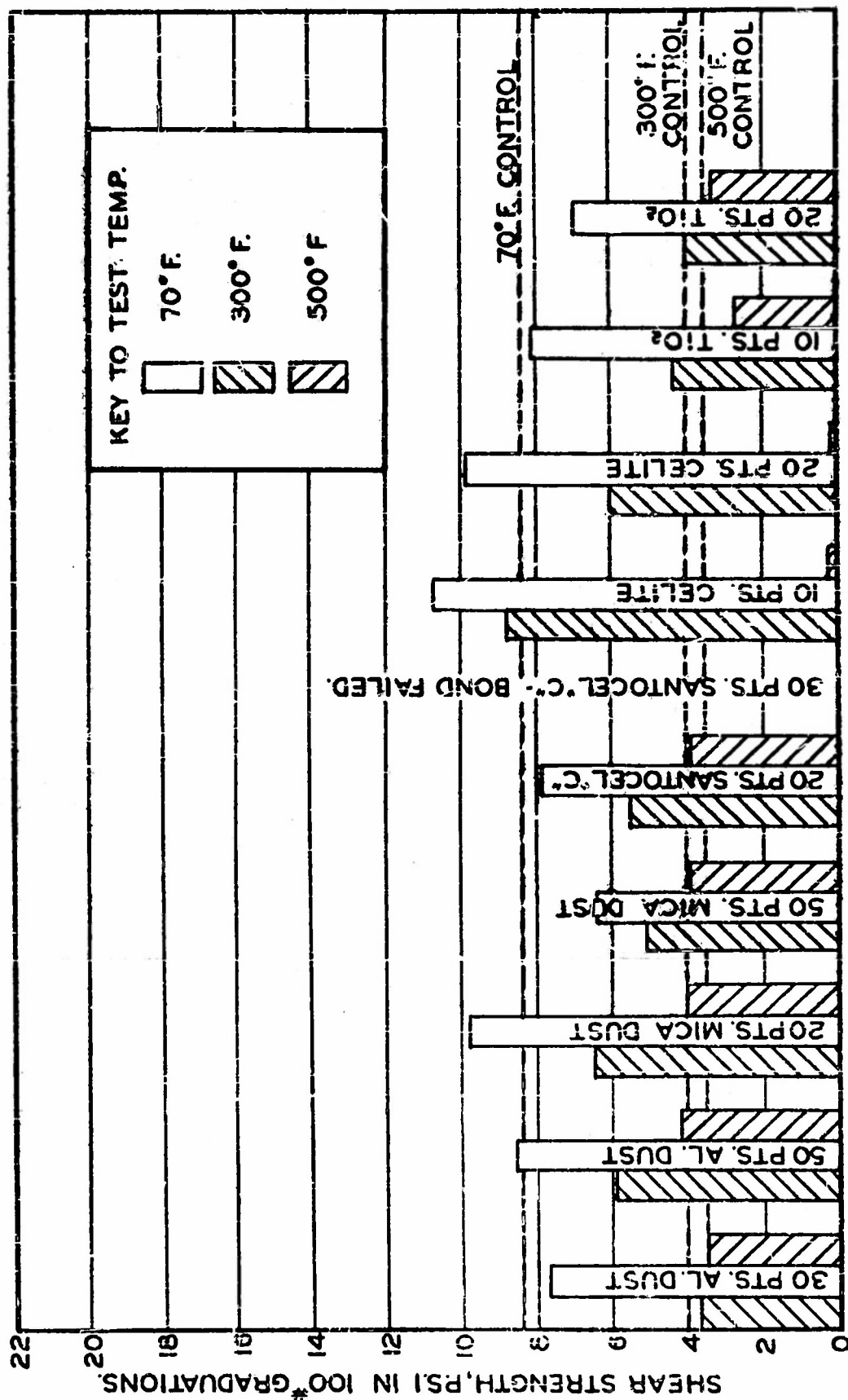


FIG.12- EFFECT OF VARIOUS FILLERS ON DC-804 SILICONE RESIN.

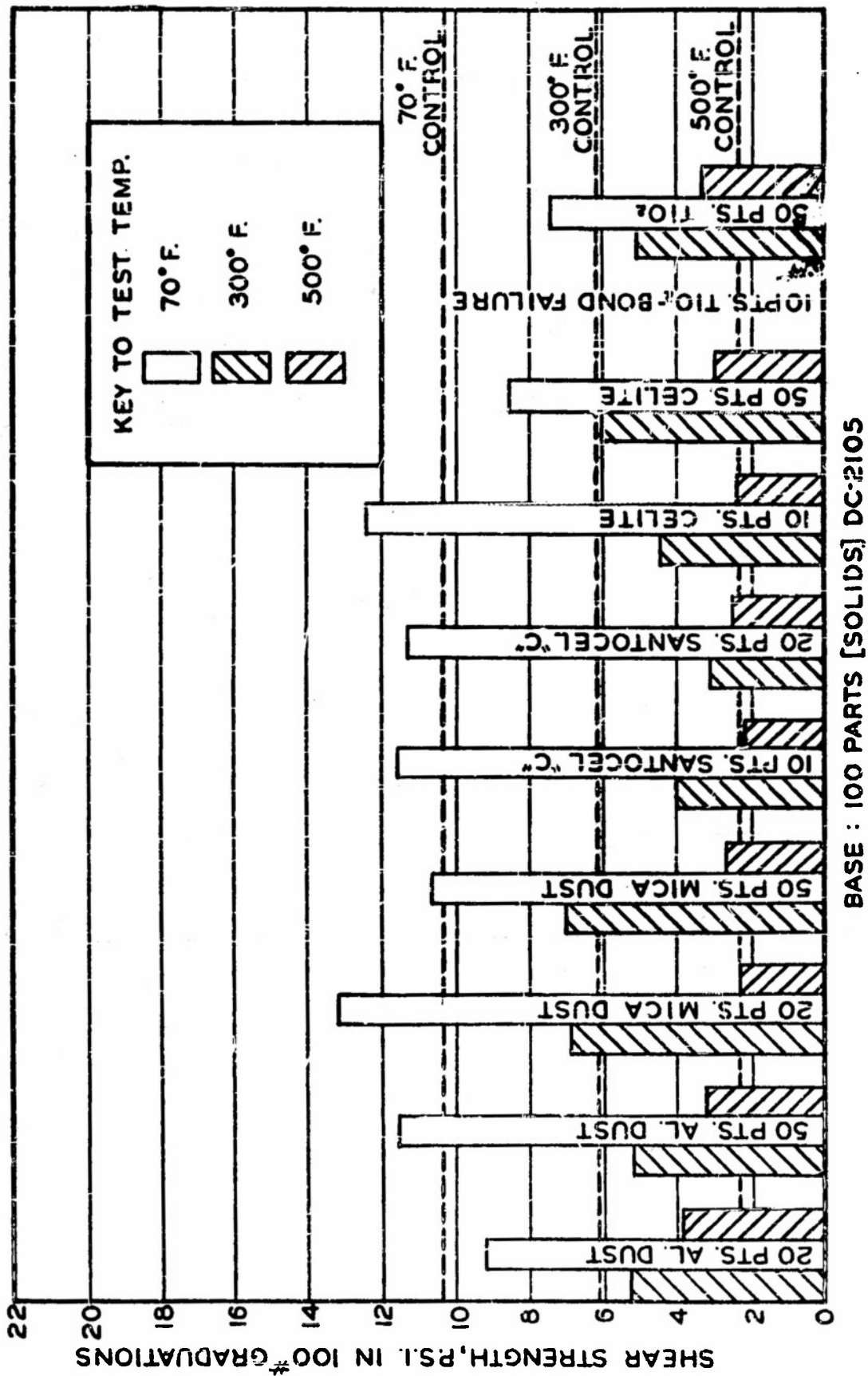


FIG.13-EFFECT OF VARIOUS FILLERS ON DC-2105 SILICONE RESIN.

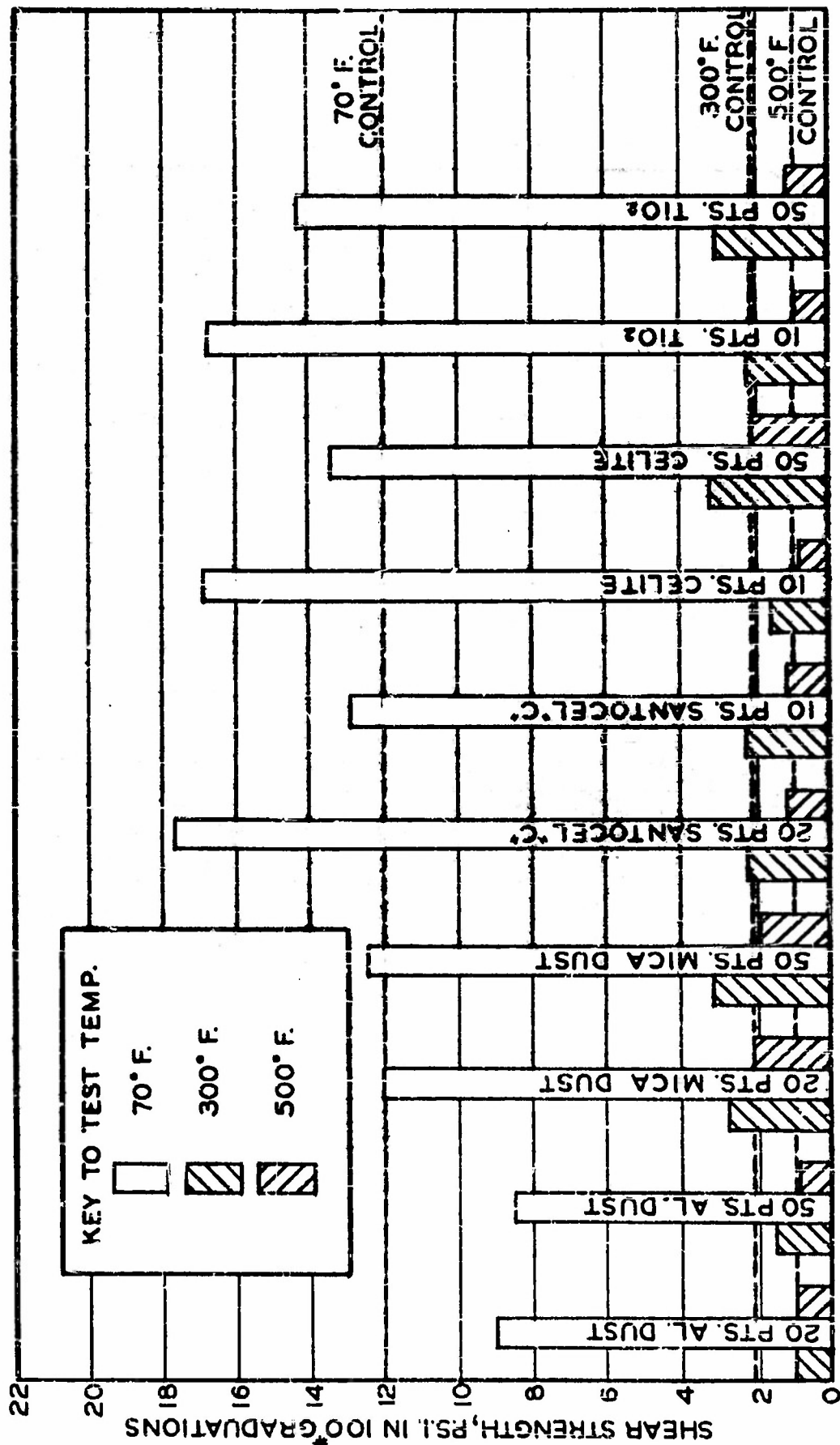
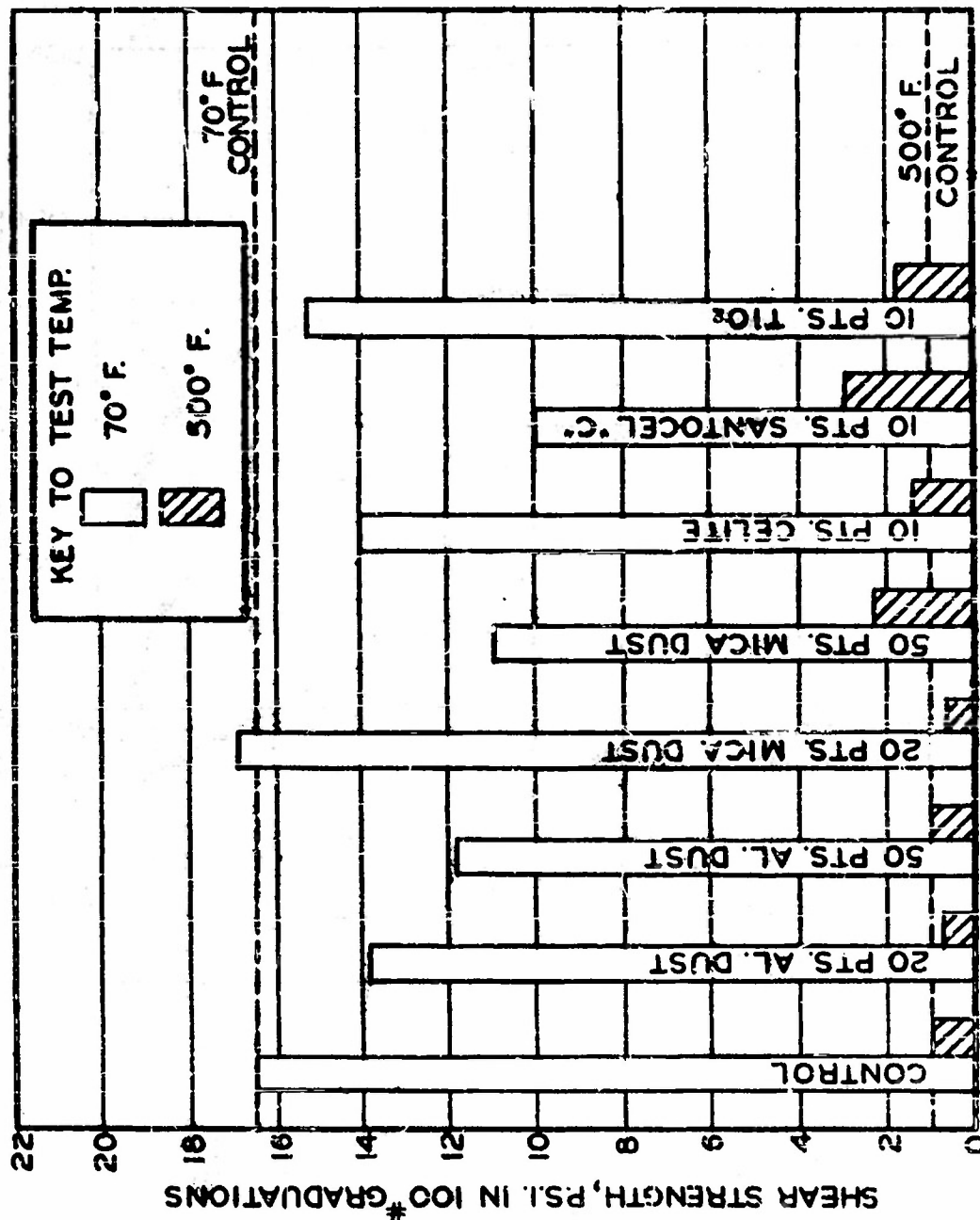


FIG.14-EFFECT OF VARIOUS FILLERS ON DC-996 SILICONE RESIN.



BASE : 100 PARTS [SOLIDS] X-2608 COPOLYMER

FIG.15-EFFECT OF VARIOUS FILLERS ON X-2608 SILICONE ALKYD RESIN.

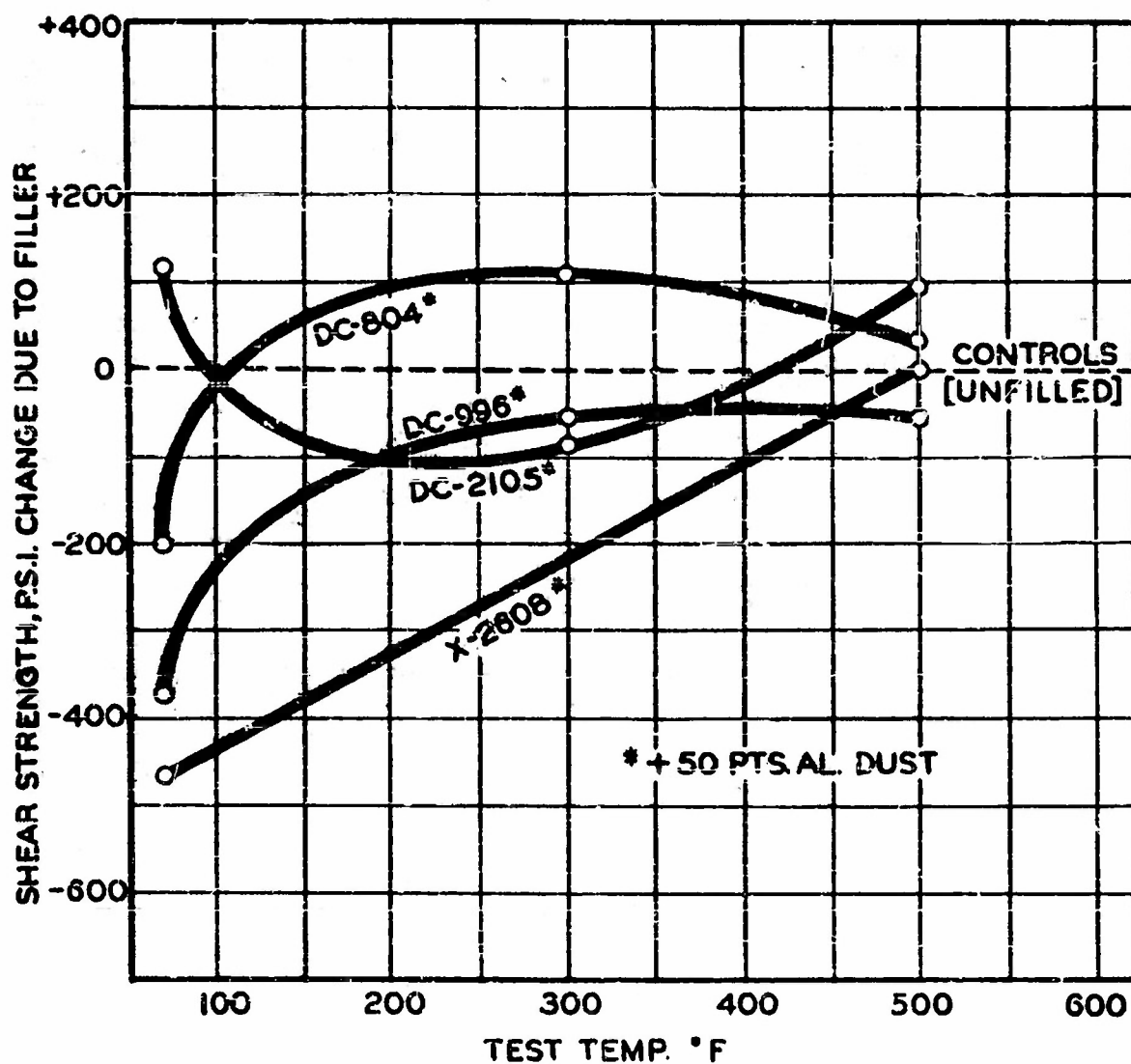


FIG.16 - THE EFFECT OF 50 PARTS ALUMINUM DUST FILLER ON HIGH TEMPERATURE SHEAR STRENGTH OF RESINS.

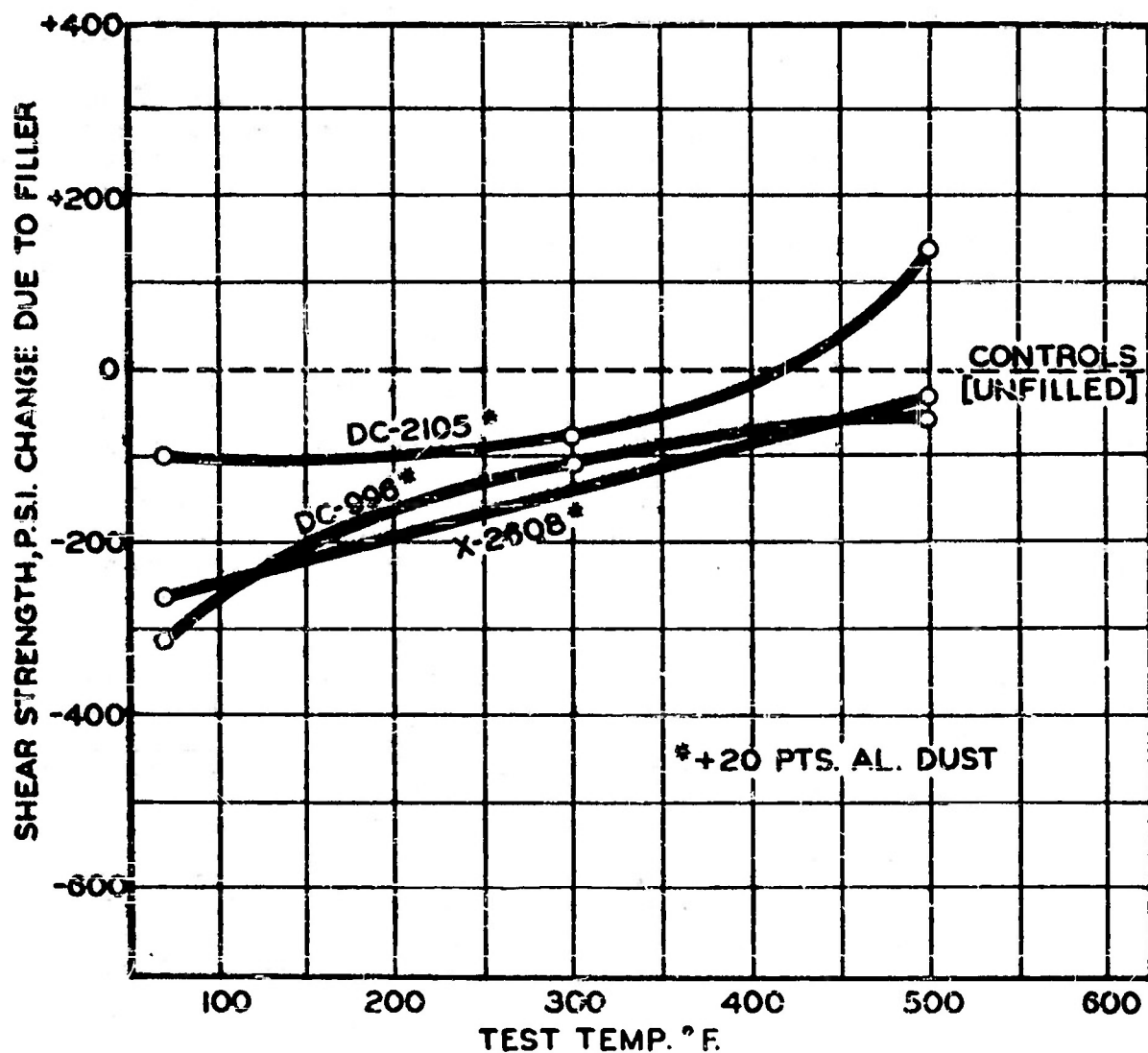


FIG.17-THE EFFECT OF 20 PARTS ALUMINUM DUST FILLER ON HIGH TEMPERATURE SHEAR STRENGTH OF RESINS.

The silicone-alkyd copolymer is made somewhat stronger at 500°F by the addition of 50 parts of mica dust or 10 parts of Santocel.

It is concluded that, though some improvement in elevated temperature strength has been obtained in some cases, the addition of fillers does not eliminate the thermoplasticity of silicone resins.

3. The Effect of Polymerization Catalysts on High-Temperature Strength of Resins

A large number of the catalysts which are widely used in the silicone resin industry were included in the investigation. These are triethanolamine, lead, iron, and zinc octoates and naphthenates (commercially known as Octasols and Uversols) and the Dow Corning Catalyst XY-15. In addition, titanates, whose effectiveness has been announced in recent patents, ^{1/} were included also. Tetra-isopropyl and tetra-n-butyl titanates were used. Catalysts were added in concentrations ranging from 0.1% to 1% to several promising resins selected for the study.

Shear strengths of nearly 1000 psi were obtained at 300°F with titanate-catalyzed DC-2103 resin. Uncatalyzed DC-2103 gave the highest single shear strength at 500°F shortly after reaching that temperature, which was 750 psi. This figure represented 81% of the room-temperature strength of that particular run (Bond #508). The contract requires 1000 psi shear strength after aging 1200 hours.

The most striking effect of a catalyst (see Table 17 and Figures 18 through 21) was the marked improvement in shear strength at both normal and elevated temperatures, which resulted from the use of tetra-isopropyl titanate and tetra-n-butyl titanate. DC-2103 resin, containing 1% of a titanate catalyst, retained 80 to 90% of its room-temperature strength at 300°F. Furthermore, the room-temperature strength, as well, was increased by the use of these catalysts (Bond #509 and 510). The addition of tetra-isopropyl titanate to DC-2105 resin brought about a marked increase in strength at both 300° and 500°F (Bond #467). The addition of 0.5% triethanolamine increased the room-temperature shear strength of DC-996, DC-804 and DC-2105 (Bonds #407, 433, 416, 419, 489). DC-804 was weakened by all the octoate and naphthenate catalysts to the extent that the bonds fell apart. Only triethanolamine was a useful catalyst for this all-methyl polymer.

^{1/} Gullledge, Hugh C. Titanated Organo-Silicon-Oxy Compounds.
Application date 5 April 1948, U.S. Patent 2,512,058.
Belgian Patent 500,963

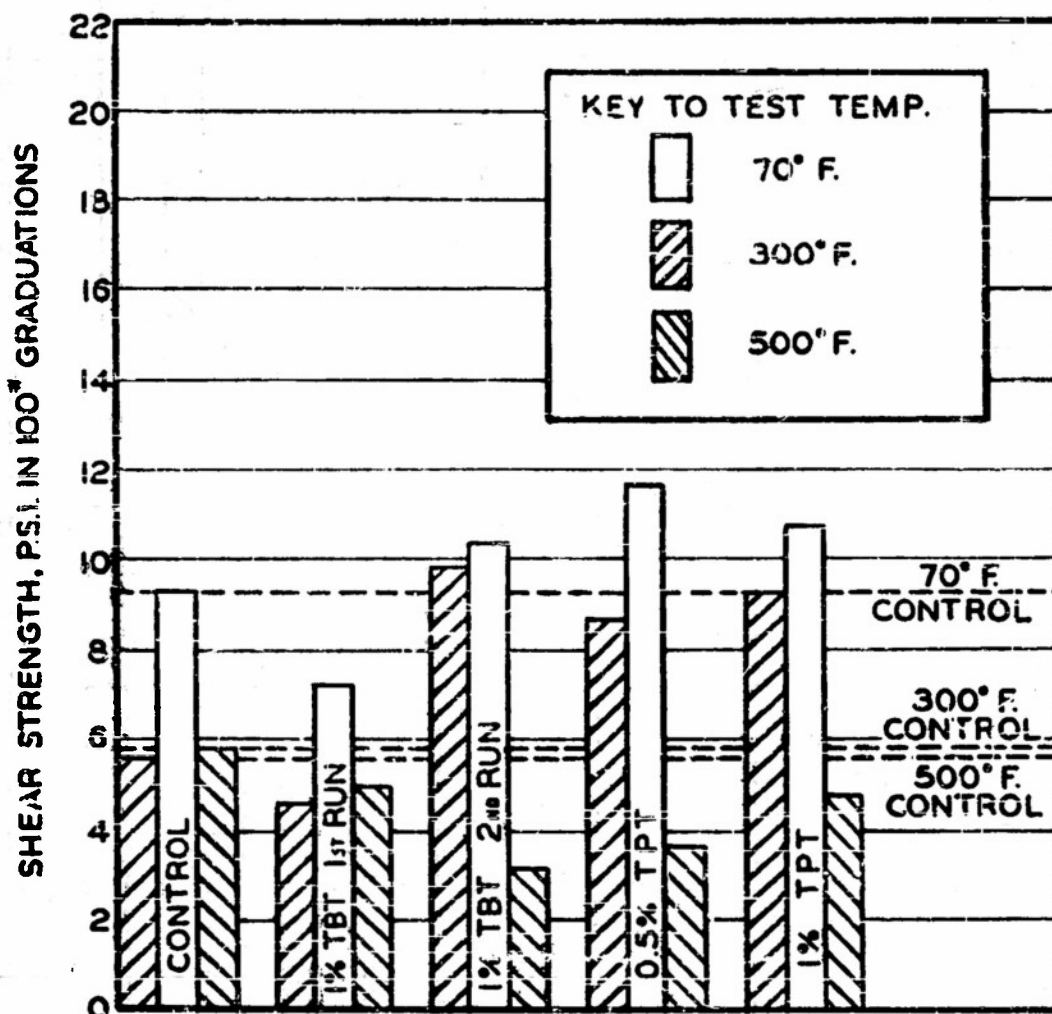
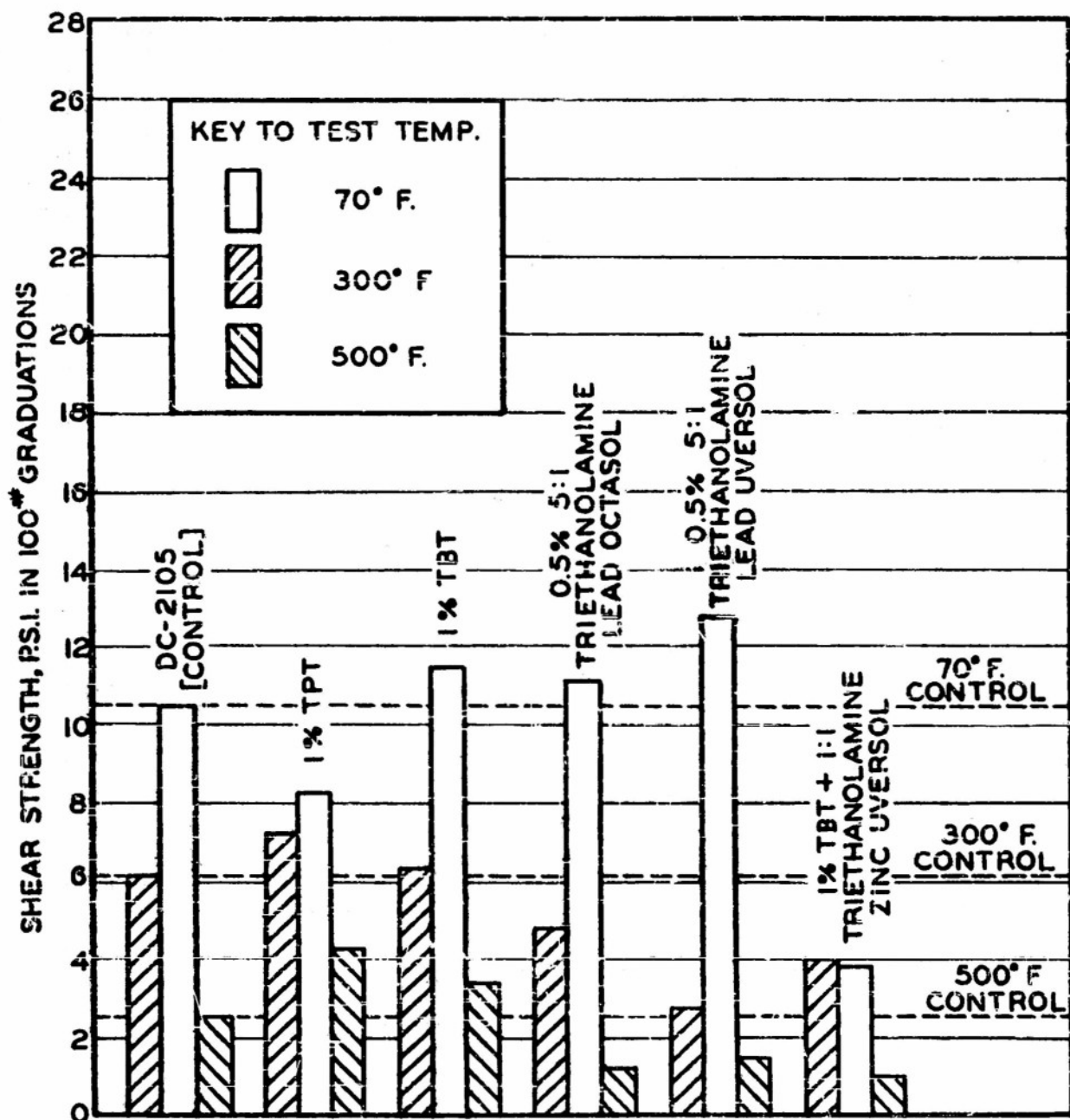


FIG.18-EFFECT OF TITANATE CATALYSTS ON DC-2103 SILICONE RESIN.



KEY : TBT = TETRA-N-BUTYL TITANATE
TPT = TETRA ISOPROPYL TITANATE
OCTASOLS = OCTOATES
UVERSOLS = NAPHTHENATES

FIG.19-THE EFFECT OF CATALYSTS ON THE HIGH TEMPERATURE SHEAR STRENGTH OF DC-2105 SILICONE RESIN.

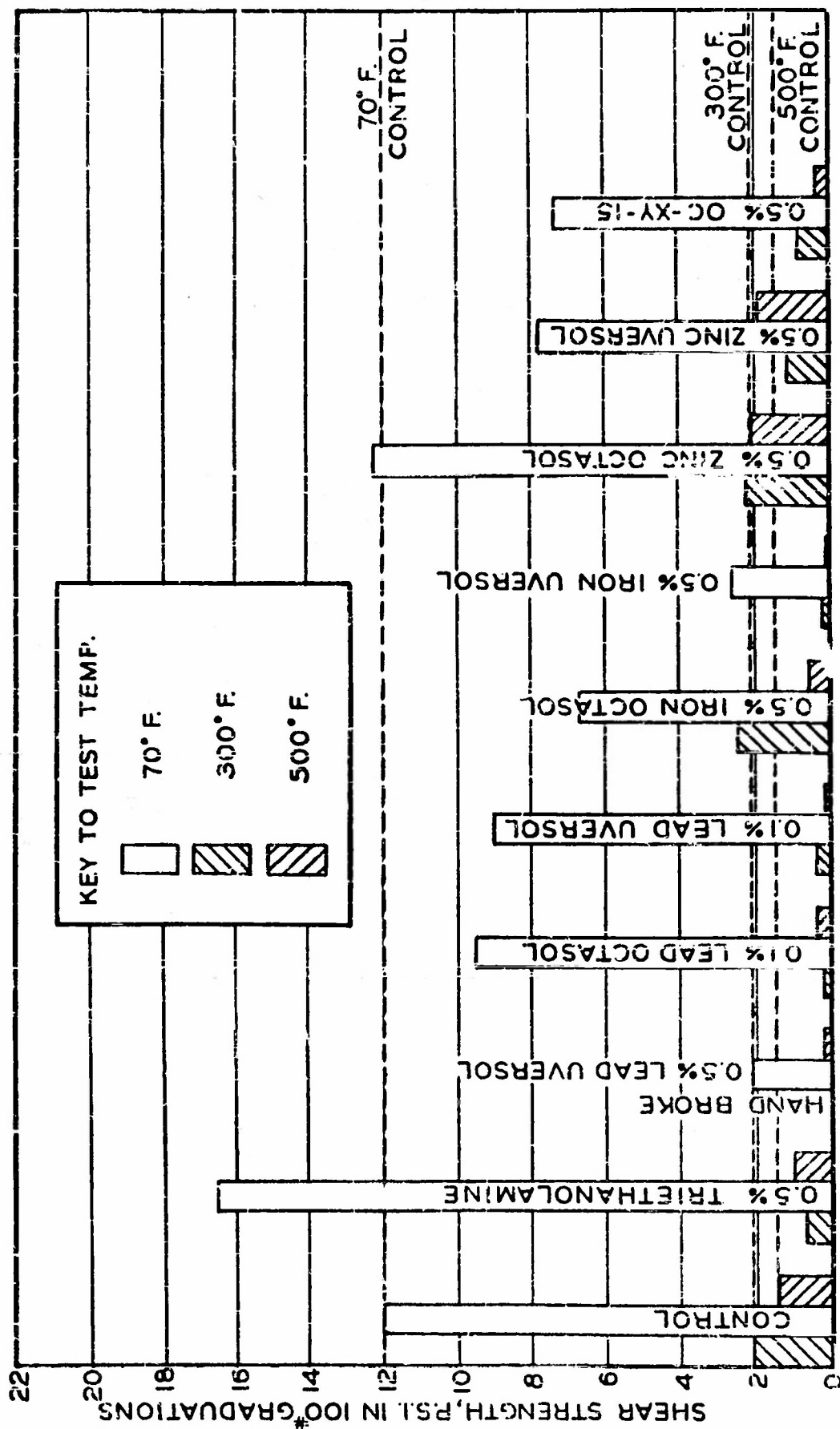
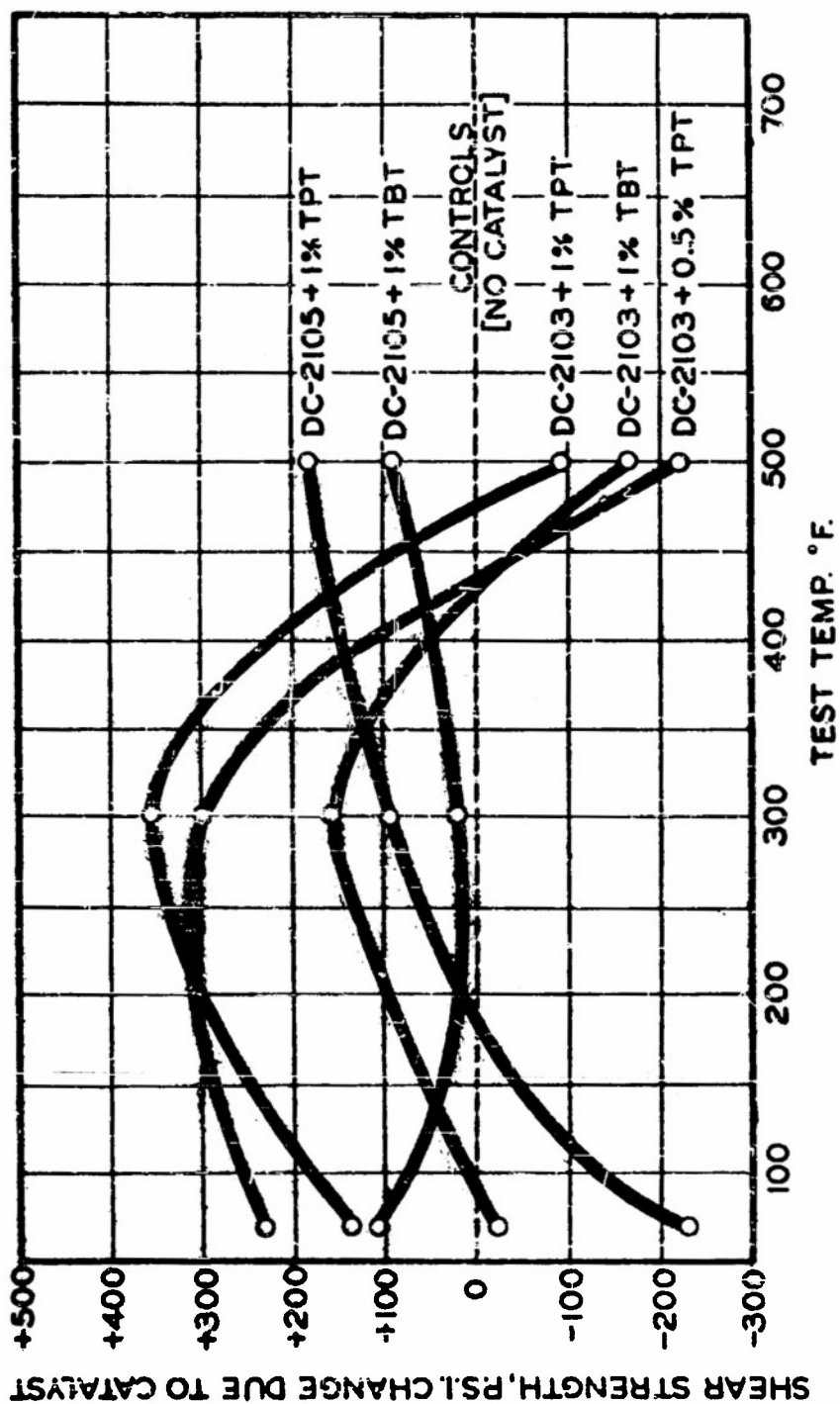


FIG.20-THE EFFECT OF VARIOUS CATALYSTS ON DC-996 SILICONE RESIN.



KEY: TBT = TETRA-N-BUTYL TITANATE
TPT = TETRA ISOPROPYL TITANATE

FIG.21-THE EFFECT OF CATALYSTS ON HIGH TEMPERATURE SHEAR STRENGTH OF DC-2105 AND DC-2103 SILICONE RESINS.

In the cases where the shear strength at room temperature is decreased by the addition of catalysts, it is thought that the catalyst promoted an excessive degree of cross-linking, rendering the resin brittle and subject to quick shattering under the strain of shear tests. It is supposed that tetra-isopropyl and tetra-n-butyl titanates promote the additional degree of cross-linking required by DC-2103 and 2105 to reduce thermoplasticity.

At present, DC-2103 and DC-2105 appear to be the most promising resins for high-temperature service, and the titanates appear to be the most promising catalysts.

Perhaps the addition of a quantity of filler plus a titanate catalyst will reduce thermoplasticity somewhat more, but probably not enough to meet requirements. A subsequent step will be to investigate the value of a certain class of titanium organics known as chelates in eliminating thermoplasticity. Certain chelates have been found by Shell Development Company to be indispensable in maintaining strength after high-temperature aging of epoxide-phenolic structural adhesives. The value of chelates has not yet been determined for the silicone structural adhesives.

E. Survey of Commercial Structural Adhesives

Several commercially available structural adhesives, known to have good strength, were tested for the purpose of evaluating the cleaning, bonding and testing techniques developed in this laboratory. The initial tests were carried out on two adhesives of the phenolic-rubber type: MN3C tape, supplied by Narco, Inc., Costa Mesa, California; and EC-1245 solution, supplied by the Minnesota Mining and Manufacturing Company, St. Paul, Minnesota. Bonds obtained by the use of these adhesives were of the proper order of strength (3000-4000 psi shear strength, room temperature).

Subsequent tests were run on the following commercial structural adhesives.

Scotchweld No. 588, a bonding film in tape form, supplied by the Minnesota Mining and Manufacturing Company.

CTL-91-D, a high-temperature phenolic resin supplied by the Warnken Engineering Company, Cincinnati, Ohio

Armstrong A-6 with Activator "E", an epoxy-type resin formulation containing a mineral-type fibrous filler and an amine catalyst, supplied by the Armstrong Products Company, Warsaw, Indiana.

SS-15 Paste, a compounded silicone rubber bonding paste, supplied by the General Electric Company, Waterford, New York.

Pliobond, an adhesive cement, supplied by the Goodyear Company.

Data on shear strength tests run on the commercial adhesives listed above may be found in Table ~~1~~. The results indicate that our laboratory techniques are comparable to those used in the industrial field. (Synco 935-C with Accelerator "N", a thermosetting resin, supplied by the Snyder Chemical Company, Bethel, Connecticut, was applied to panels in the usual fashion, but no tests were run on this material, since it was found to be too soft and pliable.)

F. Synthesis of Siloxane polymers for Structural Adhesives

1. Introduction

During the course of the program, the work has been on a trial-and-error basis as far as the selection of materials and use of adhesives was concerned. This has been due, for the most part, to the fact that the composition of commercial resins is not revealed by the manufacturers. Exact R to Si ratios or percentages of the various organic radicals present in the resin formulations would be valuable for indicating relationships, if any, of the type of organic radicals to adhesion. Physical measurements such as viscosity cannot be used as a method of characterization because the method of preparation influences the viscosity. The only reliable method of determining such relationships is by testing the adhesion of a series of silicone resins of known composition. To this end, samples of commercially available monomers were obtained and a program was set up for the preparation of monomers that were not available, and, eventually, for the preparation of a series of silicone polymers of known composition. Information for the preparation of the unavailable monomers and polymers was obtained from the literature and U.S. Patents.

2. Accomplishments

The following monomeric compounds were prepared:

- a. Tetramethyldisiloxane-1-3-diol
- b. Diphenylsilanediol
- c. Octaphenylcyclotetrasiloxane
- d. Hexaphenylcyclotrisiloxane

In addition to these, an all-methyl polymer was prepared from dimethyldichlorosilane and methyltrichlorosilane having a R:Si ratio of 1.41:1.

Recently a new patent ^{1/}has been received which describes a simplified method for the preparation of the siloxane resins, in which the number of steps is reduced. This patent has not yet been checked experimentally, but comments as to its usefulness will be included in the next report.

^{1/} Welch, Charles E., and Holdstock, Norman G. Process for Preparing Polysiloxane Resins. Application date 8 February 1951. U.S. Patent 2,661,348.

V. METHODS FOR PREPARATION AND SHEAR-TESTING OF EXPERIMENTAL STRUCTURAL ADHESIVES

The methods here described are those used throughout the research under this contract. Where variable methods were used at a particular stage of the preparation, such as priming, all the methods used are described under the key symbols listed in the tables.

A. Description of the Metals

One inch by four inch panels were used for shear tests.

A-1 Alclad aluminum 24S-T3, 0.064 inch thick

A-2 Same aluminum, 0.031 inch thick

A-3 The above aluminum (A-1) after anodizing. Aluminum was anodized by either an electrical (E-1 and E-1a) or a chemical process (E-2). The anodizing processes are described below.

SS-1 Stainless steel, 18-8 full hard, conforming to MIL-S-5059, 0.036 inch thick.

B. Preparation of the Metal Surface for Bonding

1. For Aluminum

The standard surface preparation was chromic-sulfuric acid cleaning (C-1 below) as recommended by WADC. Experimental cleaning methods where used are listed in the tables. The cleaned panels were usually primed in preparation for elastomeric adhesives, usually unprimed for resin bonding materials. All varying cases are so listed in the tables.

Some sets of experiments utilized aluminum which had been anodized to produce a surface layer of $Al(OH)_3$. This process replaced acid-cleaning. Anodic surfaces were usually "sealed" to deposit silicone molecules between the pores of aluminum hydroxide.

2. For Stainless Steel

The panels were usually cleaned by the hydrochloric-nitric acid method (C-5) recommended by WADC. Experimental cleaning methods, when used, are listed in the tables.

C. Cleaning Methods

1. For Aluminum

C-1 (Cleaning Aluminum)

Cleaning with chromic acid solutions, according to paragraph 3.1.2.2.1.1 of MIL-A-9067, recommended by WADC.

- a. Degrease by immersion for at least 16 hours in trichloroethylene at room temperature.
- b. Dip, with agitation, for 10 minutes in a chromic acid solution of the following composition by weight:

Water	30 parts
Conc. H_2SO_4	10 "
Cyrst. $Na_2Cr_2O_7$	1 "

This is to be maintained at a temperature of 150-160°F.

- c. Rinse six times with cold water and allow to dry at least 30 minutes at room temperature, or 10 minutes at 150-200°F in a circulating-air oven.
- d. The panels are stored, when necessary, in a desiccator containing a drying agent or constant humidity solution, prior to bonding.

C-2 (Cleaning Aluminum)

Recommended by Dow Corning as preparation for silicone adhesives.

a,c,d, the same as for C-1

- b. Dip five minutes in concentrated HCl at 80°F. Rinse with water. Dip 30 minutes in concentrated HNO_3 at room temperature.

C-3 (Cleaning Aluminum)

This utilizes Alumiprep, a metal cleaner of Neilson Chemical Company. It is one of the cleaning methods recommended by Midland Industrial Finishes Company.

- a. Degrease by immersion for 16 hours in trichloroethylene at room temperature.
- b. Dip in diluted (one part to two parts water) Alumiprep at room temperature for 30 seconds. Shake off excess then wipe with a cloth which has been dampened with Alumiprep. Alumiprep has an acid pH and is designed to prepare aluminum for painting. It is the counter-part of Metalprep for steel.

2. For Stainless Steel

C-5 (Recommended by WADC)

- a. Degrease by immersion for 16 hours in trichloroethylene at room temperature.
- b. Dip, with agitation, in 15 percent by weight HCl for 5 minutes at 80°F. Rinse.
- c. Dip, with agitation, in 30 percent by weight HNO₃ for 30 minutes at 80°F. Rinse.
- d. Rinse thoroughly with cold water, and dry at room temperature, or not above 200°F.

C-6 (Cleaning Stainless Steel)

This is a method specified by the Bloomingdale Rubber Company for use with their Hycar-phenolic structural adhesives of the FM-47 type.

- a. Treat for 7 minutes in the following solution, maintained at the boiling point:

Sodium Carbonate	2.0 oz/gal
Sodium Hydroxide	2.0 oz/gal
Rosin Soap	0.5 oz/gal
Alkyl Aryl Sodium Sulfonate	0.5 oz/gal
Anhydrous Sodium Metasilicate	3.0 oz/gal

- b. Treat for four minutes in the following pickling solution, maintained at room temperature:

Concentrated H ₂ SO ₄	25% by volume
Concentrated HNO ₃	25% by volume
Water	50% by volume

- c. Treat for one minute at room temperature in the following bright dip solution:

Concentrated HCl	55% by volume
30% H ₂ O ₂	2% by volume
Water	43% by volume

- d. Rinse thoroughly with cold water and dry.

C-7 (Cleaning Steel)

Use of Metalprep solution (Neilson Chemical Company). This is a proprietary mixture used to prepare steel for painting which acts as a rust-remover and paint primer. Used the same as Alumiprep.

D. Anodizing Methods (for Aluminum)

E-1 Electrical anodizing (thick anodic layer)

- a. Dip in NaOH solution (approximately $\frac{1}{2}$ lb per gal) about 30 seconds at 160° to 180°F. Cold water rinse.
- b. Dip in 60% HNO₃ solution about 30 seconds at room temperature. Cold water rinse.
- c. Anodize in 15% H₂SO₄ solution at 85°F. Raise voltage to 15 volts over five minutes and maintain 15 volts for 45 minutes at 20 amps/sq ft density. Cold water rinse.

E-1a Electrical anodizing (thin anodic layer)

- a and b same as E-1 process
- c. Anodize in 15% H₂SO₄ solution at 78° to 80°F. Raise voltage to 18 volts over five minutes and maintain 18 volts for 30 minutes at 12 to 15 amps/sq ft. Cold water rinse.

The electrical anodizing was done by Contract Plating Company of Stratford, Connecticut.

E-2 Chemical anodizing

This process was performed by Enthone Corporation of New Haven, Connecticut, and the exact procedure is not known to this company.

E. Priming Methods

P-1 (CHR-260 primer containing disilanes)

- a. After cleaning, the panels are dipped in 100%* solution of CHR-260 (in isopropyl alcohol or carbon tetrachloride) primer for approximately 30 seconds.

*Based on product as sold in isopropyl alcohol solution.

- b. Remove. Shake off excess primer. Air-dry for 30 minutes at room temperature.

P-2 CHR-260 50%* solution	Same method
P-3 CHR-260 25%* solution	" "
P-4 CHR-260 10%* solution	" "
P-5 CHR-260 1%* solution	" "
P-8 CHR-260 100%* + 0.5% H_3PO_4	" "
DC-796 (Dow Corning primer)	

Contains ethyl orthosilicate in isopropyl alcohol.

- a. Applied to cleaned panels by brushing or dipping. Excess shaken off.
- b. Air-dry at room temperature for 30 minutes to hydrolyze the primer.
- c. Rinse in cold water. Air-dry at room temperature or 150°F.

Numerous other experimental priming methods are described in the appropriate tables.

F. Sealing Methods (for anodized aluminum)

Described in the appropriate tables.

G. Application of the Adhesive and Curing

1. Elastomeric

- a. A small amount of the elastomer is pressed onto one panel, cleaned and primed. If solvent is present, it is allowed to evaporate at 70° or 150°F.
- b. Eight such panels are placed in a jig (Figure 22). A second panel is placed over the first with $\frac{1}{8}$ inch overlap. The jig is so designed that it regulates the size of the overlap area to exactly $\frac{1}{8}$ sq in. When the cover is placed on the jig, the assembled bonds are held in position without movement or slippage.

*/ Based on product as sold in isopropyl alcohol solution

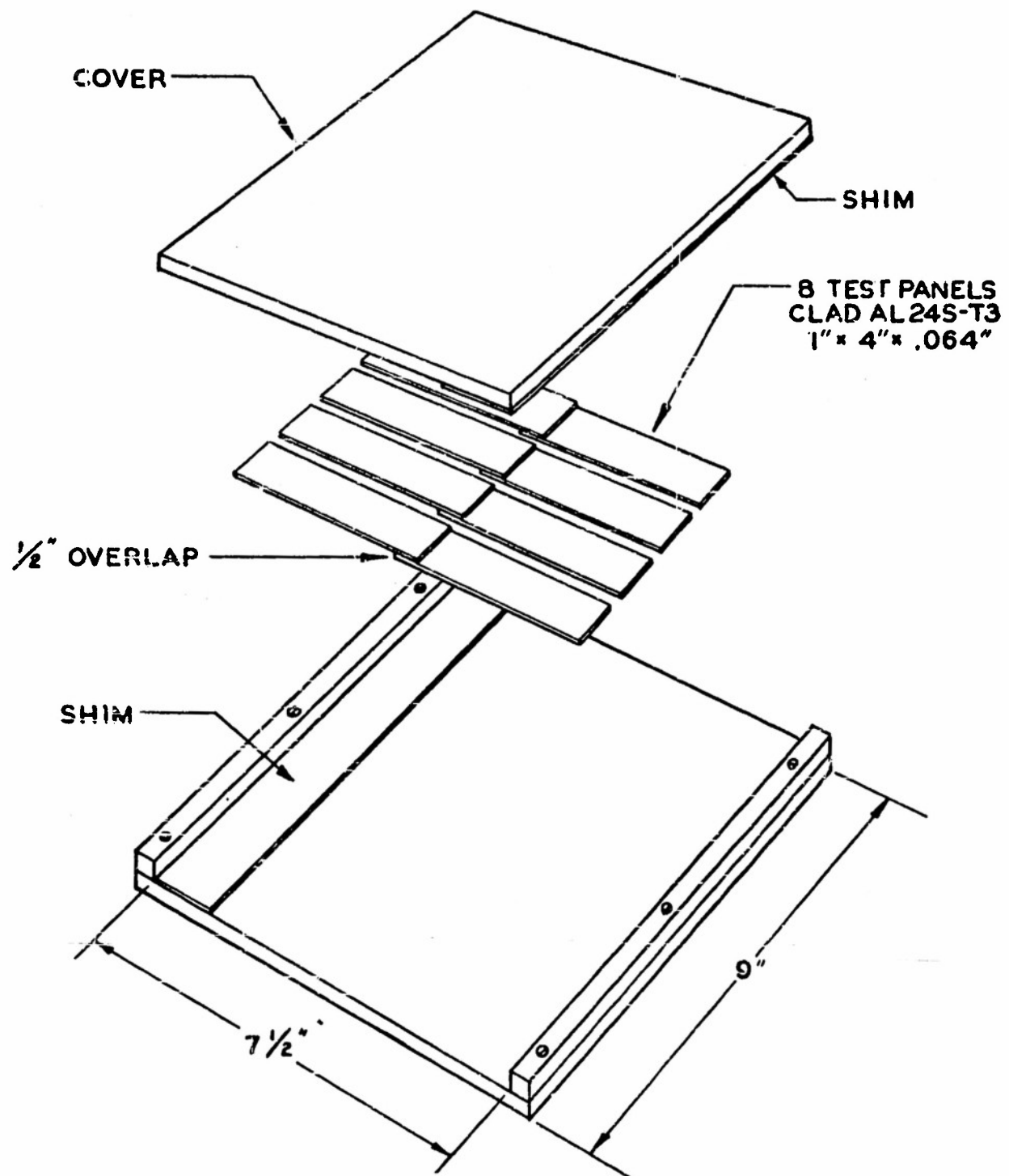


FIG.22-JIG FOR ASSEMBLING SHEAR TEST
PANELS FOR SCREENING PROGRAM.

- c. The bonds in the jig assembly are subjected to pressure, usually at 250°F for 30 minutes at 2500 psi in a Preco hydraulic press. Details of time, temperature, and pressure are given in the tables.
- d. The pressed bonds, still in the jig, are oven-cured at the temperature and times given in the tables, usually 16 hours at 300°F.

2. Resin

- a. An amount of resin in about 50% solution is painted on the overlapping portions of both panels, appropriately cleaned, and primed. The solvent is evaporated at room temperature or at 150°F.
- b. The cure of the resin is usually "advanced" before assembling, by partially curing the resins on the separate panels $\frac{1}{2}$ or 1 hour at 300°F. This procedure helps to prevent the resin from running out of the glue line during the cure of assembled bonds.

In some cases (earlier part of work), a piece of glass scrim was placed in the resin in the glue line, prior to assembling. This procedure was also intended to hold the resin in the glue line, and in these cases the cure was not "advanced".

- c. Same as step b. above for elastomer
- d. The bonded panels in the jig are placed in the Preco press at contact pressure only to cause the partially cured resin on the assembled panels to flow together, thus bonding. The exact times and temperature, usually about 30 minutes @ 300°F, are given in the appropriate tables.
- e. The bonded panels, still in the jig, are oven-cured as tabulated, usually 16 hours at 480°F.

H. Shear-Testing at Room Temperature

Shear tests were done using a Dillon Dynamometer, Model K, which operates over the range of 0 to 10,000 psi and modified to have a loading rate of 1200 to 1400 psi per minute. Most shear tests were run in quadruplicate.

J. Shear-Testing at Elevated Temperature

1. Description of Equipment

A small Multiple Unit Electric Furnace Type 123-1 of the axial-hinged tube type is affixed between the jaws of the Dillon Tester, Model K, for the purpose of heating and keeping the test panel at the elevated temperature desired while under test. This furnace was obtained from Fisher Scientific Co. and was manufactured by the Hevi Duty Electric Co. Its outside dimensions are 6½ inches diameter and 5 inches in height. The inside diameter is approximately 1½ inches to accommodate the one inch wide test panels. The heat input to the furnace is regulated by means of a powerstat to control the voltage input. The temperature of a test panel is measured by means of a copper-constantan thermocouple which is wrapped around the bonded area. The thermocouple connection is made to a Leeds Northrup Precision Potentiometer No. 8662 which is sensitive to 0.031 millivolts, a voltage change equivalent to 1°F. The conversion from millivolts to degrees Fahrenheit is made through the use of Standard Conversion Tables.

A copper-constantan thermocouple is used for testing at 500°F. For testing at 700°F, it will be necessary to use an iron-constantan thermocouple. Because of varying degrees of pre-heat of the oven, panels, jaws of the tester, and the air, it is necessary to measure the temperature in the glue line of each sample during the test. It has been found that measurement of the temperature by means of a thermocouple wrapped around the outside of the bonded area is an accurate measure of the temperature in the glue line. Several checks have been run with thermocouples both in the glue line and wrapped around the outside, and they are always within five degrees of each other. Therefore the heat of radiation from the heating element in the interior of the furnace is not sufficient to make temperature measure on the outside of the panel inaccurate.

Since the oven is five inches high, it is impossible to have the test panels grasped by the tester jaws at only four inches apart during the test as specified by the WADC test procedure. However, it can be seen from Part K which follows that elevated-temperature shear tests results obtained with our equipment agree with WADC results within 8%.

A photograph, Figure 23, shows the elevated temperature shear-testing equipment. A bonded specimen is in the jaws of the Dillon Tester within the electric furnace which is mounted on the platform of the lower jaw. The potentiometer is shown beneath the Dillon, and the powerstat appears on the shelf.

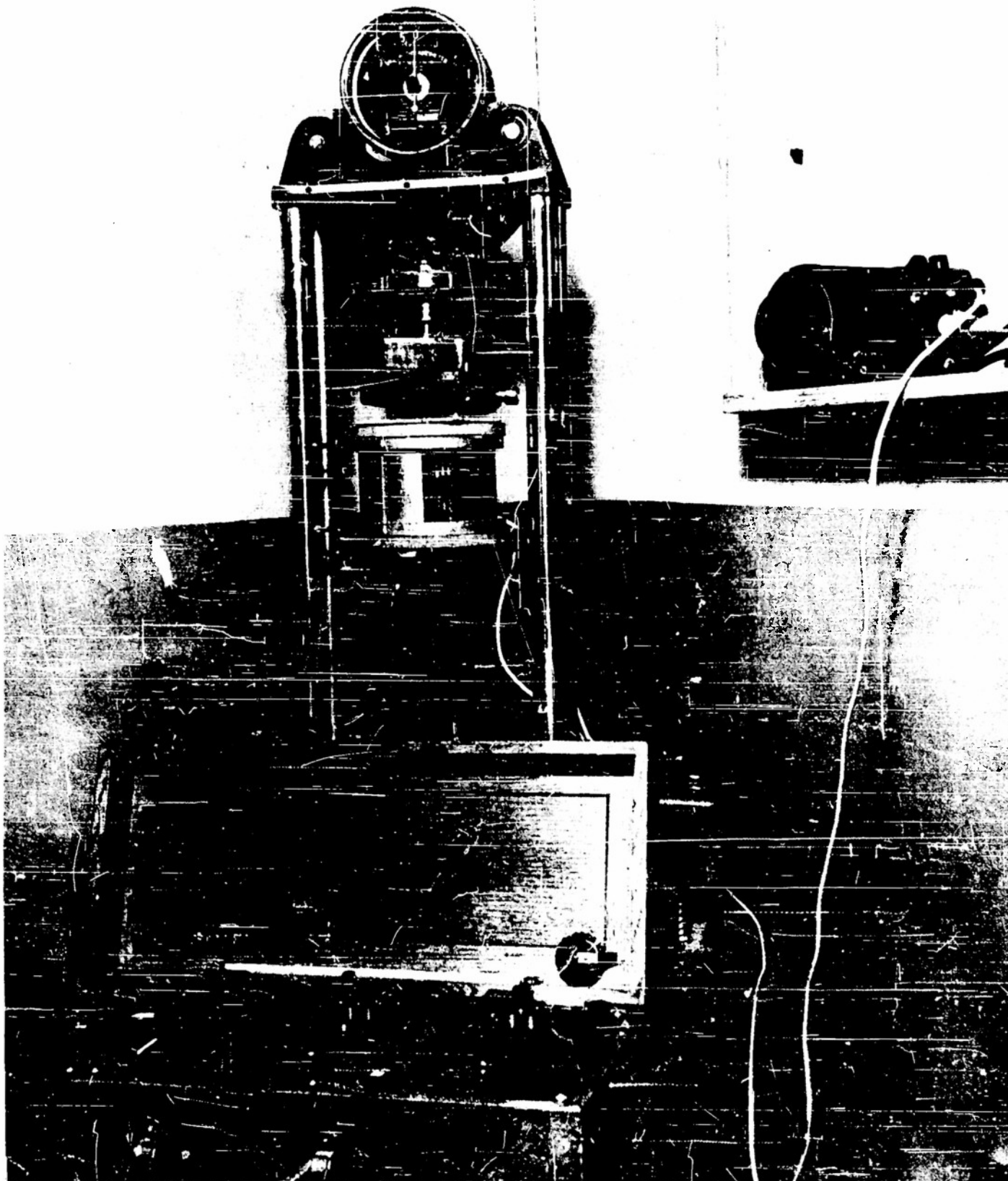


FIG. 23 HIGH TEMPERATURE SHEAR TESTING EQUIPMENT
WADC TR54-98 74

2. Procedure for Testing Strength at Elevated Temperature

The jaws of the Dillon Tester are preheated in an oven for about $\frac{1}{2}$ hour. A copper-constantan thermocouple is wrapped around the bonded area of the test panel and held on with paper clips prior to insertion in the jaws of the tester. The bonded test panel is inserted in the jaws of the tester, and the preheated electric furnace is placed on the platform of the lower jaw around the test panel. A sheet of asbestos insulation is placed on the top of the furnace to insulate the top opening of the cylindrical chamber. The powerstat is set at a reading of between 70 and 80 to obtain a temperature of 500°F in the glued area of the test sample. This temperature is equivalent to 13.25 millivolts (reference junction of 0°F) on the potentiometer. A temperature of 500°F at the glue line is maintained for five minutes before commencing the test. The temperature is never allowed to drop below 500°F but sometimes rises to a few degrees above 500°F.

High-temperature tests to date have been performed shortly after reaching the test temperature. When elevated temperature tests are performed in accordance with the contract requirements, a large oven will be used for aging the samples. Aged samples will be quickly transferred to the Dillon Tester, fitted with the Electric Furnace for shear testing.

K. Evaluation of Shear-Testing Procedures

1. The Effect of Alignment of the Test Panels During Shear Test.

This experiment was performed to determine whether or not slight misalignment of the test panels in the jaws of the Dillon Tester during the shear test affects the shear strength measurements obtained.

X-6719A was used as the adhesive, and 25% CHR-260 as the primer. Two sets of samples were tested with perfect alignment of the test panels, and two sets with misalignment as great as the relative positions of the test jaws would allow.

The results in Table 19 show that misalignment causes no observable effect on the shear test results.

2. Evaluation of Shear-Testing Technique: Comparison Between WADC and Connecticut Hard Rubber Co.

It was considered to be of value to compare the shear-testing technique used at this company with the standard technique

used at WADC. To do this, a set of 30 samples were bonded with Shell's epoxide-phenolic resin No. 422-V-28 at WADC, and a set of about 18 samples were bonded with X-6719A after CHR-260 priming at Connecticut Hard Rubber Co. In each case, half were tested at Connecticut Hard Rubber Co. and half at WADC -- some at room temperature and some at 500°F.

The shear test data in Table 20 show very good correlation between the test results of Connecticut Hard Rubber Co. and WADC. In the room-temperature shear tests, the average deviation with both bonding materials was less than 4%. With the tests at 500°F, there was a difference of only 8% between the tests at the two laboratories. In all cases, the Connecticut Hard Rubber Co.'s average shear-test results were slightly lower than those obtained at WADC.

The actual average deviation of Connecticut Hard Rubber Co. tests from WADC tests is as follows:

Shell 422-V-28

Room Temperature	-3.8%
500°F	-8.0%

Dow Corning X-6719A

Room Temperature	-2.5%
------------------	-------

It is concluded that the exchange of shear test data between Connecticut Hard Rubber Co. and WADC laboratories will be directly comparable and therefore it will not be necessary for one to recheck the other's results.

EXPLANATION OF THE TABLES

Key numbers are used throughout the tables to describe cleaning, priming, and anodizing methods. These methods are described in the section of this report titled "Methods for Preparation and Shear-Testing of Experimental Structural Adhesives."

TABLE - 1

EVALUATION OF SILICONE ELASTOMERS AS EXPERIMENTAL
STRUCTURAL ADHESIVES FOR ALUMINUM

Panel Set No.	Clean- ing Method	Prim- ing Method	Adhesive Compo- sition	Cure				Avg. Glue Line Thick- ness, Mils	Avg. Shear Strength, psi @ 70° F	Bond Adh%	Failure Con%
				Press	° F	Oven	° F				
				Hr.	lbs. Plate Pressure	Hr.	lbs. Plate Pressure				
324	C-1	P-4	GE-SS-64	1/2	250	16	300	3.5	287	0	100
325	"	"	DC-110	"	"	"	"	7.5	437	0	100
326	"	"	DC-112	"	"	"	"	8	374	0	100
31	"	P-1	SS-15	"	"	2	480	5	232	50	50
32	"	"	"	2,500	"	"	"	"	"	"	"
32	"	"	"	1/2	250	10	480	12	0	100	0
34	"	"	"	5,000	"	"	"	"	"	"	"
21	"	"	CHR-251	1/2	250	72	480	7	100	50	50
21	"	"	"	2,000	"	None	"	3	134	"	"
26	"	"	"	"	"	4 1/2	300	4	308	"	"
22	"	"	CHR-259	"	"	20	480	"	"	"	"
25	"	"	"	"	"	None	"	3	128	"	"
25	"	"	"	"	"	4 1/2	300	4	178	"	"
48	"	"	XC-270	"	"	20	480	"	"	"	"
48	"	"	"	1	300	4	300	No Bonds	"	"	"
49	"	"	XC-276	8,000	"	"	"	No Bonds	"	"	"
24	"	"	XC-6708	"	"	"	"	No Bonds	"	"	"
24	"	"	"	1/2	250	None	"	3	111	100	0
30	"	"	XC-6708	2,000	"	"	"	"	"	"	"
30	"	"	(23% Solids)	1/2	250	2	265	3	55	100	0
33	"	"	"	2,500	"	2	470	"	"	"	"
33	"	"	"	1/2	250	10	480	12	0	100	0
140	"	None	Chlorinated Silicone IX	5,000	"	"	"	"	"	"	"
140	"	"	"	1/2	250	12	300	3	285	0	100
141	"	P-4	"	"	"	"	"	3	300	0	100
136	"	None	Chlorinated Silicone XVII	"	"	"	"	3	0	50	50
23	"	P-1	X-6719A	1/2	"	None	"	3	80	100	0
23	"	"	"	2,000	"	"	"	"	"	"	"

TABLE - 1 (Contd.)

Panel Set No.	Cleaning Method	Priming Method	Adhesive Composition	Cure Press		Oven		Avg. Glue Line Thickness, Mils	Avg. Shear Strength, psi, 70°F	Bond Adh%	Failure Coh%
				Hr.	°F.	Hr.	°F.				
130	C-1	10% Chlorinated Silicone XVII ¹	X6719A	1/2	250	12	300	3	330	75	25
135	"	"	"	"	"	"	"	2	405	80	20
27	"	P-1	X6719A (50% Solids)	"	"	20	480	2	200	100	0
35	"	"	"	1/2	250	72	480	3	80	100	0
29	"	"	X6719A (30% Solids)	1/2	250	4 1/2	300	4	240	100	0
28	"	"	X6719A (15% Solids)	"	"	"	"	3	270	"	"
137	"	None	X6719A+ 50pts Chlorinated Silicone XVII	1/2	250	12	300	2	205	30	70
138	"	P-4	"	"	"	"	"	2	300	80	20
193	"	"	X6719A+ 20pts. GS1993	"	"	17	300	3	205	100	0
194	"	"	"	"	"	24	480	1	50	"	"
195	"	"	X6719A+ 20pts. Santocel C	"	"	16	300	2	290	"	"
196	"	"	"	"	"	24	480	1	10	"	"
197	"	"	X6719A+ 20pts. Cabot Aero-sil Silica	"	"	16	300	3	275	"	"
198	"	"	"	"	"	24	480	3	230	"	"
189	"	"	X6719A on Glass Scrim	"	"	"	"	3	125	"	"

TABLE I - (Contd.)

Panel Set No.	Clean- ing Method	Prim- ing Method	Adhesive Compo- sition	Cure		Avg. Glue Line Thick- ness, Mils	Avg. Shear Strength psi. 70° F	Bond Adh. %	Failure Coh. %		
				Press	Oven						
				Hr. °F	Hr. °F						
190	G-1	P-4	Same as 189+ 1 coat 10% X6719A Soln.	1/2	250	24	480	3	275	100	0
191	"	"	Same as 189 scrim primed with CHR 260	"	"	"	"	"	95	"	"
192	"	"	Same as 191+ 1 coat 10% X6719A Soln.	"	"	"	"	"	325	70	30

Footnote;

- The chlorinated silicones were chlorinated General Electric SE-76 (polydimethylsiloxane)
 IX Cl atoms; Si atoms = 1.49:1
 XVII " " " = 1.32:1

All other adhesive compositions mentioned are described in the Appendix

TABLE - 2

EVALUATION OF X6719-A ADHESIVE ON STAINLESS STEEL

Panel Set No. ¹	Clean- ing Method	Prim- ing Method	Adhesive Composi- tion	Cure		Glue Line Strength,		Avg. Shear Thickness, .psi @ °F Mils	Bond Adh%	Failure Coh%
				Press Hr.	Oven °F	Press Hr.	Oven °F			
115	C-5	P-4	X6719-A (100%)	1/2	250	12	275	3	853 70	50 50
116	"	"	"	"	"	"	"	5	875 70	75 25
118	C-6	"	"	"	"	1	300	2	442 70	100 0
120	"	"	"	"	"	"	"	2	510 70	100 0
122	Metlprep Soln.	"	"	"	"	"	"	2	320 70	70 30
114(A-D)	C-5	"	"	"	"	"	"	3	405 75 ²	100 0
114(E,F)	"	"	"	"	"	"	"	4	260 527 ²	100 0
114(G,H)	"	"	"	"	"	"	"	3	230 387 ²	100 0

Notes:

1. Test panels of 0.036 in. 18-8 steel (MIL-S-5059), 1 in. x 4 in.
2. Thermocouple on front of panel for 114(E,F) and on back of panels for 114 (G,H).

TABLE - 3

THE EFFECT OF PRIMERS ON SHEAR STRENGTH
OF ELASTOMERIC STRUCTURAL ADHESIVES ON ALUMINUM

Panel Set No. ¹	Clean- ing Method ²	Prim- ing Method ²	Adhesive Compo- sition	Cure		Avg. Glue Line Thick- ness, Mils	Avg. Shear Strength, psi @ 70°F	Bond Failure	
				Press Hr. °F	Oven Hr. °F			Adh% Coh%	
54	C-1	DC-796	X6719-A $\frac{1}{2}$ (50% Solids)	250	None	No Bonds			
57A	"	"	"	"	None	1	3	100	0
62A	"	DC-796+ H ₂ O wash	"	"	4 300	7	92	50	50
62B	"	DC-796	"	"	"	7	80	100	0
57B	"	"	"	"	16 "	10	40	"	"
55	"	"	"	"	4 " + 4 480	13	7	"	"
57C	"	"	"	"	16 "	5	154	"	"
60(A)	"	"	"	"	"	7	10	"	"
58A	"	P-1	"	"	None	10	9	"	"
63A	"	P-1 + H ₂ O wash	"	"	4 300	7	162	0	100
63B	"	P-1	"	"	"	7	142	100	0
58B	"	"	"	"	16 "	10	9	"	"
64A	"	"	"	"	"	3	0	"	"
66A	"	"	"	"	"	4	126	50	50
68A	"	"	"	"	18 "	6	700	100	0
56	"	"	"	"	4 " + 4 480	1	21	"	"
70A	"	"	"	"	"	5	350	"	"
58C	"	"	"	"	16 "	15	74	"	"
61	"	"	"	"	"	5	168	"	"
64B	"	P-2	"	"	" 300	4	80	"	"
66B	"	"	"	"	"	6	49	"	"
68B	"	"	"	"	18 "	6	1025	50	50
70B	"	"	"	"	4 480	6	450	100	0
65A	"	P-4	"	"	16 300	4	185	50	50
67A	"	"	"	"	"	4	0	100	0
69A	"	"	"	"	18 "	5	550	50	50
71A	"	"	"	"	4 480	6	750	"	"
83A	C-2	"	"	"	60 300	2	468	100	0
65B	C-1	P-5	"	"	16 "	4	155	50	50
67B	"	"	"	"	"	6	20	100	0
69B	"	"	"	"	18 "	5	730	50	50
71B	"	"	"	"	4 480	5	600	100	0
85	C-2	DC-796	X 6719-A	"	20 300	4	670	70	30
87	C-1	"	"	"	"	4	610	"	"
89	C-2	"	"	"	"	5	590	"	"

TABLE - 3 (Contd.)

Panel Set No. ¹	Cleaning Method ²	Priming Method ²	Adhesive Composition	Cure		Avg. Glue Line Thickness, Mils	Avg. Shear Strength, psi @70°F	Bond Failure	
				Press Hr.	Oven °F			Adh% Coh%	
109	C-1	P-4	X 6719-A 1/2	250	12 300	10	440	100	0
110	C-2	"	"	"	"	13	390	"	"
101	"	"	"	"	16 "	4	930	80	20
102	C-1	"	"	"	"	4	740	50	50
84	C-2	"	"	"	20 "	1	313	100	0
92	None	"	"	"	"	4	350	"	"
83B	C-2	"	"	"	60 "	3	900	"	"
97	C-1	"	"	"	84 "	8	650	80	20
98	C-2	"	"	"	"	11	780	50	50
111	C-1	"	"	"	2 480	15	270	100	0
96	"	P-8	"	"	16 300	3	400	"	"
86	C-2	"	"	"	20 "	4	720	70	30
88	C-1	"	"	"	"	3	710	"	"
90	C-2	"	"	"	"	4	670	"	"
93	C-1	None	"	"	16 "	3	270	75	25
300	"	"	"	"	"	6	685	50	50
303	"	"	"	"	"	4	715	"	"
306	"	"	"	"	"	5	312	100	0
91	None	"	"	"	20 "	5	380	"	"
164	C-1	1 coat 10% X6719-A cured 10 min @300°F	"	"	12 "	2	850	70	30
163	"	P-4+as in 164	"	"	"	2	800	"	"
178	"	SE-100	"	"	"	4	250	100	0
179	"	CHR-259	"	"	"	3	415	"	"
180	"	"	"	"	"	3	205	"	"
170	"	2 coats 10% X6719-A cured 10 min @300°F	"	"	"	3	175	"	"
171	"	Same as 170 except cure 1 hr @300°F	"	"	"	3	240	"	"
172	"	Same as 170 except cure 1 hr @480°F	"	"	"	4	295	"	"
185	"	2 coats 10% X 6719-A cured 1 hr @300°F each	"	"	15 "	4	530	"	"
186	"	4 coats as per 185	"	"	"	3	515	"	"
187	"	P-4 + 185	"	"	"	3	500	"	"
188	"	P-4 + 186	"	"	"	3	530	75	25
173	"	P-4 + 170	"	"	12 "	3	45	100	0

TABLE - 3 (Contd.)

Panel Set No. ¹	Clean- ing Method ²	Priming Method ²	Adhesive Compo- sition	Cure		Avg. Glue Line Thick- ness, Mils	Avg. Shear Strength, psi. @70°F	Bond Failure			
				Press Hr.	Oven °F			Adh%	Coh%		
174	C-1	P-4+171	X6719-A	1/2	250	12	300	2	50	100	0
175	"	P-4+172	"	"	"	"	"	3	175	"	"
299	"	S -32	"	"	"	16	"	5	35	"	"
302	"	DC-996	"	"	"	"	"	6	156	"	"
305	"	DC-994	"	"	"	"	"	6	35	"	"
298	"	P-4+299	"	"	"	"	"	7	35	80	20
301	"	P-4+302	"	"	"	"	"	4	40	90	10
304	"	P-4+305	"	"	"	"	"	7	30	100	0
124	"	SiCl ₄ , 1% in CCl ₄ + H ₂ O wash	"	"	"	12	"	1	297	"	"
126	"	"	"	"	"	"	"	2	237	"	"
134	"	"	"	"	"	"	"	3	620	"	"
129	"	TiCl ₄ , 1% in CCl ₄ + H ₂ O wash	"	"	"	"	"	3	440	50	50
133	"	"	"	"	"	"	"	3	455	80	20
181	"	CH ₃ SiCl ₃ , 5% in CCl ₄ + NH ₄ OH wash	"	"	"	15	"	3	430	100	0
183	"	CH ₃ SiCl ₃ , 10% in CCl ₄ + NH ₄ OH wash, 1 coat 10% X6719-A cured @ 300°F	"	"	"	12	"	4	850	"	"
182	"	(CH ₃) ₂ SiCl ₂ , 5% in CCl ₄ + NH ₄ OH wash	"	"	"	15	"	3	300	"	"
184	"	(CH ₃) ₂ SiCl ₂ , 10% in CCl ₄ + NH ₄ OH wash, 1 coat 10% X6719-A cured @ 300°F	"	"	"	"	"	4	280	"	"
94	"	Sodium Silicate, 3%	"	"	"	16	"	4	150	75	25
125	"	Sodium Silicate, 1%	"	"	"	12	"	3	290	100	0
148	"	Sodium Methyl Siliconate	"	"	"	18	"	3	10	"	"
251	"	P-4 after sur- face treatment 2% benzoyl per- oxide, brush on from isopropyl alcohol solution	"	1	"	24	480	8	108	"	"

TABLE - 3 (Contd.)

Panel Set No.1	Clean- ing Method2	Priming Method2	Adhesive Compo- sition	Cure				Avg. Glue Line Thick- ness, Mils	Avg. Shear Strength, psi @ 70°F	Bond Failure	
				Press Hr.	Oven °F	Press Hr.	Oven °F			Adh%	Coh%
298	C-1	P-4+SR-323	X 6719-A	1/2	250	16	300	7	35	80	20
299	"	SR-323	"	"	"	"	"	5	35	100	0
300	"	None	"	"	"	"	"	6	685	50	50
301	"	P-4+DC-9963	"	"	"	"	"	4	40	90	10
302	"	DC-9963	"	"	"	"	"	6	156	100	0
303	"	None	"	"	"	"	"	4	715	50	50
304	"	P-4+DC-9943	"	"	"	"	"	7	30	100	0
305	"	DC-9943	"	"	"	"	"	6	35	100	0
306	"	None	"	"	"	"	"	5	312	100	0

Notes:

1. All panels were A-1 aluminum
2. Cleaning methods C-1 and C-2 and priming methods P-1 through P-6 are described in detail in Section VI of this report.
3. Resin layer was exposed at 150°F for 1 hour to completely evaporate the solvent and at 350°F for 1 hour to partially cure before rubber was applied. Resin primer layer was kept down to one mil thickness. Resins were applied as 10% xylene solutions.

TABLE - 4

EVALUATION OF ANODIZING AND SILICONE SEALING
AS SURFACE PREPARATION OF ALUMINUM
(X6719-A Elastomeric Adhesive Used for all Tests)

Panel Set No.	Anodizing or Clean- ing Method	Priming or Seal- ing Method	Cure				Avg. Glue Line Thick- ness, Mils	Avg. Shear Strength psi @ 70°F	Bond Adh%	Failure Coh%
			Press Hrs.	Oven °F	Press Hrs.	Oven °F				
153	E-1	No Sealing	1/2	250	13	300	3	460	100	0
166	"	"	"	"	"	"	2	480	"	0
151	"	GE 81119 oil	"	"	12	"	2	680	"	0
159	"	#151 + H ₂ O Seal	"	"	"	"	-	4100	50	50
154	"	Dimethyl Tetra- mer+air dry	"	"	"	"	3	570	100	0
165	"	Dimethyl Tetra- mer contn. catalyst for polymerization	"	"	"	"	2	725	"	0
168	"	#165 + H ₂ O Seal	"	"	"	"	1	155	"	"
155	"	GE SM-61 Oil Emulsion	"	"	13	"	3	130	"	"
149	"	Linde GS-1 Resin Emulsion	"	"	12	"	2	220	"	"
150	"	#149 sealed 30 min.	"	"	"	"	3	300	"	"
169	"	G-2 Silicone Oil, 10%	"	"	"	"	3	180	"	"
152	"	CHR 260 10%, not sealed	"	"	13	"	3	200	"	"
156	"	#152-3 coats	"	"	15	"	5	270	"	"
157	"	CH ₃ SiCl ₃ , 3 coats, H ₂ O wash, air dry between coats	"	"	"	"	2	150	0	100
158	"	(CH ₃) ₂ SiCl ₂ , Same as #157	"	"	"	"	4	110	"	"
160	"	(C ₆ H ₅) ₂ Si(OH) ₂ , 3%, dried, H ₂ O sealed	"	"	13	"	2	270	60	40
160A	"	"	"	"	56	"	2	130	"	"
244 ²	C-1	P-4	"	"	16	"	5	473	100	0
263	C-3	None	1	250	"	"	9	145	100	"
243	None	None	2	"	"	"	9	80	100	"
246	E-1a	GE Silicone oil 81119 ³	"	"	"	"	6	115	100	"
247	"	GE SF-96(500) ³	"	"	"	"	4	160	100	"

TABLE - L (Contd.)

Panel Set No.	Anodizing or Cleaning Method	Priming or Sealing Method	Cure			Avg. Glue Line Thickness, Mils	Avg. Shear Strength, psi @ 70°F	Bond Failure	
			Press Hrs.	°F	Oven Hrs.	°F		Adh %	Coh %
248	E-1a	GE Silicone oil 81392 ⁶	1/2	250	16	300	4	207	100 0
252	"	Dimethyltetramer ³	1	"	"	"	8	250	100 "
270	C-1	Dimethyltetramer ³ + P-4	1/2	"	"	"	8	400	90 10
280	E-1a	Dimethyltetramer, Catalyzed with potassium isopropoxide ^{3,4}	"	"	"	"	3	75	100 "
281	"	3% Soln. diphenyl-silenediol in acetone 10 min. Room temp. H ₂ O sealed 30 min @ 212°F	"	"	"	"	4	480	100 "
282	"	3% Soln. diphenyl-silenediol in acetone 10 min @ room temp.	"	"	"	"	5	206	100 "
283	"	3% Soln. diphenyl-silenediol in toluene 10 min @ 212°F	"	"	"	"	12	110	100 "
284	"	Same as 283 plus H ₂ O sealed 30 min. @ 212°F	"	"	"	"	22	175	100 "
289	"	GE 81392 ³ + 1% benzoyl peroxide ⁵	"	"	"	480	16	100	100 "
249	"	GE 81392 + 0.1% benzoyl peroxide ⁵	"	"	"	"	8	200	100 "
290	"	"	"	"	"	"	9	100	100 "
291	"	GE 81392 ³ + 10% benzoyl peroxide ⁵	"	"	"	"	4	141	100 "
142	E-2	GE 81119 oil, light	"	"	12	300	4	130	50 50
142A	"	"	"	"	"	"	4	490	100 0
142B	"	GE SF-96 oil, heavy	"	"	"	"	4	110	50 50
142C	"	"	"	"	"	"	4	465	100 0

Notes:

1. Contact pressure only.
2. Clad aluminum (A-1)
3. Immersed 10 min. @ 250°F, excess wiped off, allowed to dry, checked for water repellancy to verify that panels were sealed.
4. Catalyst prepared by heating a solution of KOH in anhydrous isopropyl alcohol 10 min. @ 250°F.
5. After oil sealing the benzoyl peroxide was brushed on from isopropyl alcohol solution.

TABLE - 5

SILICONE RESINS: THE EFFECT OF TIME OF CURE
AT 480°F ON THE PHYSICAL CONDITION

Resin	Physical Condition After Cure						Color	Foaming
	1 hr. @ 300°F	1	2 hrs @ 480°F	4 hrs. @ 480°F	8 hrs. @ 480°F	16 hrs. @ 480°F	48 hrs. @ 480°F	
General								
Electric								
81369	Hard, brittle		unchanged	unchanged	unchanged	unchanged	unchanged	None
813903	Soft		Hard, some flexibility	Hard, less flexibility	Hard	Hard	Hard, little flexibility	None
81397	Soft		Hard, some flexibility	unchanged	unchanged	unchanged	unchanged	None
SR-02	Hard, brittle		Hard, very brittle	unchanged	unchanged	unchanged	unchanged	None
SR-17 ³	Sticky		Soft, flexible	Harder, less flexible	Harder, less flexible	Harder, less flexible	Hard, some flexibility	None
SR-28	Tacky		Very sticky	Sticky	Less sticky	Soft	unchanged	None
SR-32	Sticky		Soft	Hard, flexible	Harder, flexible	Hard, less flexible	Hard with least flexibility	None
SR-53	Hard		Hard, brittle	unchanged	unchanged	unchanged	unchanged	None
SR-61	Soft		Hard, brittle	unchanged	unchanged	unchanged	unchanged	Considerable
SR-80	Hard, brittle		Hard, brittle	unchanged	unchanged	unchanged	unchanged	None
SR-82	Soft		Hard, very brittle	unchanged	unchanged	unchanged	unchanged	Considerable
SR-98	Soft		Hard, brittle	unchanged	unchanged	unchanged	unchanged	None

TABLE - 5 (Contd.)

Resin	1 Hr. @ 300° F	2 Hrs. @ 480° F	4 Hrs. @ 480° F	8 Hrs. @ 480° F	16 Hrs. @ 480° F	48 Hrs. @ 480° F	Color	Foaming
Dow Corning								
801	Soft	Hard, very brittle	unchanged	unchanged	unchanged	unchanged	Clear	Considerable
802	Tacky	Soft	unchanged	Harder, less flexible	Hard, less flexible	Hard, brittle	Clear	Minor
803	Soft	Hard, brittle	unchanged	unchanged	unchanged	unchanged	Clear	Considerable
804	Soft	Hard, brittle	unchanged	unchanged	unchanged	unchanged	Clear	Considerable
935	Sticky	Soft	Harder, some flexibility	Harder, less flexibility	Harder, less flexibility	Harder, little flexibility	Lt. Straw	None
993	Soft	Soft	Harder, some flexibility	unchanged	unchanged	Hard, little flexibility	Clear	Minor
994	Soft	Soft	Harder, some flexibility	unchanged	unchanged	Hard, flexible	Lt. Straw	None
996	Soft	Hard, some flexibility	Harder	Hard	Hard	unchanged	Dk. Straw	None
1088	Hard, brittle	Very hard brittle	unchanged	More brittle	More brittle	Very hard, brittle	Brown	None
1089	Hard, brittle	Very hard brittle	unchanged	Brittle, opaque	More brittle	Very hard, brittle	Dk. Brown	None
2103	Hard, brittle	Very brittle	--	Foamed	--	--	Clear	Foamed
2104	Soft, brittle	Hard, brittle	unchanged	unchanged	unchanged	unchanged	Clear	Minor
2105	Soft, brittle	Hard, brittle	unchanged	unchanged	unchanged	unchanged	Lt. Straw	Considerable

TABLE - 5 (Contd)

Resin	1 hr. @ 300°F	2 hrs. @ 480°F	4 hrs. @ 480°F	8 hrs. @ 480°F	16 hrs. @ 480°F	48 hrs. @ 480°F	Color	Foaming
XR-100	Hard, brittle	Hard, very brittle	unchanged	unchanged	Minor foaming	unchanged	Clear	Minor
XR-261	Hard	Very hard, brittle	unchanged	unchanged	unchanged	unchanged	Clear	Considerable
XR-398 ³	Soft	Hard, fairly flexible	unchanged	Less flexible	Less flexible	Hard, brittle	Straw	None
XR-856	Soft	Hard, little flexibility	unchanged	Harder	Harder	Hard, brittle	Straw	None
XR-807	Soft, flexible	unchanged	unchanged	Harder, less flexible	Harder, less flexible	Hard, little flexibility	Dk. brown	None
Lird ² X-612	Soft	unchanged	unchanged	unchanged	Harder, little flexibility	flexibility unchanged	Dk. Straw	Minor
X-62	Soft	Soft	unchanged	Harder, little flexibility	Harder	Hard, brittle	Dk. Straw	Considerable
X-63	Soft	Hard, brittle	unchanged	unchanged	unchanged	unchanged	Straw	Considerable
Y-104 ³	Tacky	Soft, very flexible	Harder, less flexible	Hard, less flexible	Harder, less flexible	Hard, little flexibility	Straw	None
Y-104 ³	Sticky	Hard, very flexible	Harder, less flexible	Harder, less flexible	Harder, less flexible	Hard, little flexibility	Brown	None
X-14-A	Tacky	unchanged	Soft	Harder	Hard, brittle	unchanged	Dk. Straw	None
X-14-B-64	Liquid	unchanged	unchanged	Curing on surface - liquid on the bottom	on the bottom	unchanged	Dk. Straw	None
X-14-C	Hard, brittle	--	--	Foamed	Foamed	---	Straw	Foamed

Notes:

1. To insure complete solvent evaporation.
2. Partially "set up" in the bottle.
3. Flexibility decreases gradually and steadily as the length of cure increases up to 48 hours with these resins.

TABLE - 6

SILICONE RESINS: THE EFFECT OF SHORT CURING CYCLE
ON THE PHYSICAL CONDITION

Physical Condition After Each Step of Cure Cycle

Resin	Catalyst ¹	16 hrs. @150°F ²	Plus 1/2 hrs. @300°F	Plus 1 hr. @300°F	Plus 1 1/2 hrs. @450°F
GE 81369	No	Soft	Soft but brittle	Brittle	Hard, brittle
"	Yes	Soft but brittle	Hard, brittle	Hard, brittle	Hard, brittle
GE 81397	No	Tacky	Soft	Soft	Fairly hard-some flexibility
"	Yes	Gelled	Soft solid	Solid	Hard, some flexibility
SR 80	No	Soft but brittle	Soft but very brittle	Hard, brittle	Hard, brittle
"	Yes	Hard, flexible	Hard, brittle	Hard	Hard, less brittle
DC 996	No	Tacky	Very soft	Soft	Hard, some flexibility
"	Yes	Soft	Soft solid	Harder	Hard, flexible
SR 32	No	Tacky	Soft, somewhat tacky	Sticky	Soft solid
"	Yes	Soft	Soft	Soft solid	Solid, flexible
DC 2105	No	Soft but brittle	Soft but brittle	Soft but brittle	Hard
"	Yes	Solid, brittle	Hard, flexible	Hard	Hard
SR 28	No	Very tacky	Tacky	Tacky	Tacky
"	Yes	Tacky	Tacky	Sticky	Soft sticky solid
DC-803	No	Soft but brittle	Soft but brittle	Hard, brittle	Hard, brittle
"	Yes	Solid, flexible	Hard, some flexibility	Hard	Very hard, brittle

1. 0.5% triethanolamine.
2. To insure complete solvent evaporation.

TABLE - 7

MODIFIED SILICONES AND COPOLYMERS:
THE EFFECT OF EXTENT OF CURE ON THE PHYSICAL CONDITION

Silicone Resin Copolymer ¹	Physical Condition After Cure				
	1 Hr. @ 150°F	1 Hr. @ 300°F	2 Hrs. @ 450°F	4 Hrs. @ 485°F	6 Hrs. @ 480°F
X-2605 Alkyd Fluid	Fluid	Semi-Solid	Solid, cured	Same	Same; hard, brittle
Oil Modified					
160-30-D Alkyd	"	"	"	"	Same; fairly flexible
Oil Modified					
X-2608 Alkyd	"	"	"	"	Same; hard, brittle
X-2720 Epoxy	"	"	Semi-solid	Solid, cured	Same; flexible
X-2292 Phenolic	"	Semi-solid, tacky	Solid-cured	Same	Same; flexible
V-552 Modified Silicone	Slightly fluid, tacky	Same	"	"	Same; fairly flexible
160-29-H Clear Silicone	Soft, foamed	Semi-solid	"	"	Same; hard, brittle
V-548 Modified Silicone	Slightly fluid	Solid, cured	Same	"	Same; hard, brittle
RS-556 Alkyd Modified	Fluid	Semi-solid	Solid, cured	"	Same; hard, brittle
RS-513 Alkyd	"	Semi-solid, very tacky	Semi-solid	Solid, cured	Same; hard, brittle
160-25-D Clear Silicone	Semi-solid, very tacky	Same	Same	Same	Same ³

Notes:

1. Compositions are listed as designated by the supplier, Midland Industrial Finishes Co.
2. To insure complete solvent evaporation and prevent foaming.
3. Remained uncured and tacky after 36 hours @ 480°F.

TABLE - 8

ROOM TEMPERATURE EVALUATION OF SILICONE RESINS
AS STRUCTURAL ADHESIVES FOR ALUMINUM

Panel Set No.	Clean- ing Method	Prim- ing Method	Adhesive Compo- sition	Cure		Avg. Glue Line Thick- ness, Mils	Avg. Shear Strength, psi @70°F	Bond Failure Adh% Coh%	
				Press	Oven				
				Hr. °F lbs. Plate Pressure	Hr. °F				
5	C-1	DC-796	DC-801	1 300	None	7	106	100	0
9	"	"	"	1 300	"	7	0	"	"
				3,000					
13	"	"	"	" " "	"	6	0	"	"
6	"	"	DC-802	1 300	"	7	308	"	"
10	"	"	"	1 300	"	7	0	"	"
				3000					
14	"	"	"	1 300	"	5	40	"	"
				25,000					
7	"	"	DC-803	1 300	"	7	194	"	"
11	"	"	"	1 300	"	7	50	"	"
				3000					
15	"	"	"	1 300	"	7	0	"	"
				25,000					
8	"	"	DC-804	1 300	"	7	0	"	"
12	"	"	"	1 300	"	8	100	"	"
				3000					
16	"	"	"	1 300	"	5	170	"	"
				25,000					
1	"	"	DC-935	3/4 300	1/2 490	1	0	"	"
2	"	"	"	None	3/4 400	1	0	"	"
					1 480				
17	"	"	DC-2103	1 300	None	1	0	"	"
				25,000					
18	"	"	DC-2104	" " "	"	1	0	"	"
19	"	"	DC-2105	" " "	"	1	0	"	"
20	"	"	SR-02	1 300	"	7	128	"	"
40	"	P-1	DC-935	1 300	"	7	0	"	"
				25,000					
41	"	"	DC-993	" " "	"	7	0	"	"
42	"	"	DC-994	" " "	"	3	0	"	"
43	"	"	DC-996	" " "	"	6	50	"	"
36	"	"	SR-28	1 300	"	1	36	50	50
				3,000					
44	"	"	"	1 500	"	4	36	"	"
				25,000					
37	"	"	SR-32	1 300	"	1	60	"	"
				3,000					

TABLE - 8 (Contd.)

Panel Set No.	Cleaning Method	Priming Method	Adhesive Composition	Cure		Avg. Glue Line Thickness, Mils	Avg. Shear Strength, Bond Failure		
				Press Hr. °F lbs. Plate Pressure	Oven Hrs. °F		psi @ 70°F	Adh%	Coh%
45	C-1	P-1	SR-32	1 500 25,000	None	3	107	50	50
38	"	"	SR-61	1 300 3,000	"	1	60	"	"
46	"	"	"	1 500 25,000	"	3	194	"	"
39	"	"	SR-82	1 300 3,000	"	1	269	"	"
47	"	"	"	1 500 25,000	"	3	20	"	"
216	"	P-3	SR-32 ²	None	2 500	20	920	"	"
217	"	"	DC-801 ²	"	" "	12	820	70	30
218	"	"	DC-802 ²	"	" "	11	820	80	20
219	"	"	DC-993 ²	"	" "	9	910	50	50
104	"	P-4	SR-82	1/2 250	16 300	2	595	30	70
103	C-2	"	"	" "	" "	3	430	90	10
106	"	"	DC-803	" "	" "	4	600	70	30
108	"	"	"	" "	" "	4	210	60	40
105	C-1	"	"	" "	" "	4	686	70	30
107	"	"	"	" "	" "	6	460	60	40
226B	"	"	GE-81397 ²	None	1 500	Brittle	Hand Broken		
227	"	"	SR-61 ²	"	1 450	Hand Broken ³			
228	"	"	SR-82 ²	"	" "	"			
229	"	"	DC-803 ²	"	" "	6	260 ³	90	10
230	"	"	DC-804 ²	"	" "	3	145	"	"
231	"	"	DC-996 ²	"	" "	8	515	"	"
232	"	"	DC-2104 ²	"	" "	6	260	"	"
233	"	"	DC-2103 ²	"	" "	--	Hand Broken ³		
234	"	"	DC-2105 ²	1/2 300	" "	--	" "		
253	"	None	DC-996	" "	23 480	10	1600	100	0
254	"	P-4	"	" "	21 480	8	1900	"	"
255	"	"	SR-32	" "	23 480	4	945	"	"
256	"	"	"	" "	48 "	4	1440	"	"
257	"	"	"	" "	72 "	4	1350	"	"
258	"	None	DC-996	Note ⁴	16 "	10	1830	"	"
261	"	P-4	"	"	20 "	4	1825	"	"
262	"	None	"	"	" "	4	1350	"	"
266	"	P-4	DC-802	"	*	6	1375	"	"
267	"	None	"	"	*	4	1275	"	"

TABLE - 8 (Contd.)

Panel Set No.	Cleaning Method	Priming Method	Adhesive Composition	Cure		Avg. Glue Line Thickness, Mils	Avg. Shear Strength, psi @ 70°F	Bond Failure	
				Press Hr. °F lbs. Plate Pressure	Oven Hr. °F			Adh%	Coh%
268	C-1	P-4	DC-994	Note ⁴	*	7	1460	100	0
269	"	None	"	"	*	7	1500	"	"
285	"	P-4	X-61	"	†	2	850	"	"
286	"	None	"	"	†	5	975	"	"
287	"	P-4	X-62	"	†	2	1480	"	"
288	"	None	"	"	†	7	1300	"	"
292	"	None	81390	"	16 480	7	925	"	"
293	"	P-4	"	"	"	5	990	"	"
265	"	"	"	"	"	8	1750	"	"
295	"	None	SR-17	"	"	6	950	"	"
297	"	P-4	"	"	"	5	900	"	"
362	"	"	"	"	"	4	1050	"	"
318	"	"	SR-61	"	" 5	3	450	"	"
319	"	None	"	"	" 5	2	265	"	"
320	"	P-4	SR-98	"	"	6	565	"	"
321	"	None	"	"	"	6	780	"	"
264	C-3	"	SR-32	"	36 "	14	570	"	"
265	"	"	DC-996	"	" "	7	1920	"	"
273	"	"	SR-32	"	72 "	21	1040	"	"
274	"	"	DC-996	"	72 "	25	1440	"	"
275	"	"	SR-32	"	" "	3	1000	"	"
276	"	"	DC-996	"	" "	10	1700	"	"
277	"	Dimethyl-tetramer ⁶	SR-32	"	" "	5	1000	"	"
278	"	"	DC-996	"	" "	16	900	Adhesion not complete	

Notes:

1. Test panels were A-1 aluminum.
2. With glass scrim.
3. Resin ran.
4. For all panel sets numbered above 250 the handling prior to joining and oven curing was as follows: The separate panels, painted with resin, were heated a minimum of two hours at 150°F to insure complete solvent evaporation plus 1/2 hour at 300°F to "advance" the cure. Panels were placed in jig and joined. Those which were not still soft at this point were placed in the press at contact pressure at 300°F to soften the resin and join the bonded area prior to curing at 480°F.

*Approximate oven cure was:

- 4 hours @ 480°F
- +20 hours @ 550°F
- +24 hours @ 600°F
- +20 hours @ 650°F

+ Cured @ 480°F: 6 hrs. in jig
+14 hrs. out of jig.

5. Cure advanced 3/4 hour at 300°F.
6. 10 minutes @ 250°F.

TABLE - 9

ROOM TEMPERATURE EVALUATION OF MODIFIED SILICONES
AND COPOLYMERS AS STRUCTURAL ADHESIVES FOR ALUMINUM

Panel No.	Prim- ing	Adhesive Composition ¹	"Advance" Cure Hrs. °F	Press. °F	Cure Oven Hrs. °F	Avg. Glue Line Thick- ness, Mils	Avg. Shear Strength, psi @ 70°F	Bond Failure Adh. Conf.
335	P-4	X-2605 Silicone Alkyd, Oil Modified	2 300	1/2	300 15	480	487	100 --
336	"	160-30-D Silicone Alkyd, Oil Modified	" "	" "	" "	"	1437	100
337	"	X-2608 Silicone Alkyd	" "	" "	" "	"	1492	100
338	"	X-2720 Silicone Epoxy	" "	" "	" "	"	1597	100
343	"	X-2292 Silicone Phenolic	" 250	" "	" "	"	257	40 6C
353	"	Repeat of 343	" "	" "	" "	"	502	100
344	"	V-552 Modified Silicone	" "	" "	" "	"	500	100
345	"	160-29-H Clear Silicone	" "	" "	" "	"	877	100
346	"	V-548 Modified Silicone	" "	" "	" "	"	310	100
347	"	RS-556 Silicone Alkyd, Modified	" "	" "	" "	"	1585	100
348	"	RS-513 Silicone Alkyd	" "	" "	" "	"	1575	100
311	"	Y-1043 Silicone Styrene	1/2 300	" "	" "	"	1050	100
312	None	Y-1043 Silicone Styrene	" "	" "	" "	"	1130	100
313	P-4	Y-1044 Silicone Styrene	" "	" "	" "	"	1400	100
314	None	Y-1044 Silicone Styrene	" "	" "	" "	"	1330	100

Notes:

- Y-1043 and Y-1044 were obtained from Linde Air Products Co.; the remaining resins were from Midland Industrial Finishes Co. The compositions are listed as designated by the suppliers.
- All panels were A-1 aluminum cleaned by the C-1 chromic-sulfuric acid method.
- Solvent evaporated first 1 1/2 to 2 hrs. @ 150°F. "Advance" curing is partially curing panels in the bonding position to hold the resin in the glue line.
- Contact pressure.

TABLE - 10

HIGH TEMPERATURE SHEAR STRENGTH OF SILICONE RESINS

Panel Set No.		Adhesive Composi- tion: Resin	Shear Strength, psi @70°F			Shear Strength, psi @300°F			Avg.% Thermal Effici- ency?	Shear Strength, psi@500°F			Avg.% Thermal Effici- ency?
1st	2nd		1st	2nd	Avg.	1st	2nd	Avg.		1st	2nd	Avg.	
383	402	G.E. 81359	490	1100	1100 ¹	No Bond	550	550 ¹	50	No Bond	240	240 ¹	22
365 ²		81390	1750							90			5
384	403	81397	1035	1025	1030	650	700	675	66	375	370	375	36
364 ²		SR-17	1050							50			5
319		SR-61	275							40			3
385		SR-80	No Bond										
386	404	SR-82	750	770	760	410	520	465	61	305	150	230	30
321		SR-98	770							200			26
		Dow Corning											
401	416	DC-40-C	870	760	815	450	370	410	50	325	240	290	36
387	405	DC-801	1445	1290	1370	370	520	445	32	120	240	180	13
388		DC-802	1455			70			5	100			7
389		DC-803	1450			690			48	270			19
415	418	DC-804	830	850	840	400	320	360	43	340	375	360	43
340		DC-935	1200							50			4
356		DC-993	1900							50			3
390		DC-994	1170			60			5	100			9
406	427	DC-996	1340	1070	1205	200	220	210	17	160	140	150	12
495		DC-997	785			300			38	120			15
391	436	DC-1088	950	1100	1025	200	250	225	22	90	60	75	7
396	437	DC-1089	760	1470	1115	210	320	265	24	120	60	90	8
497	503	DC-1360	1760	2550	2155	220	600	410	19	150	110	130	6
395	438	DC-2103	1120	1120	1120	980	820	900	80	450	420	435	39
392	440	DC-2104	700	740	720	400	540	470	65	280	280	280	39
393	441	DC-2105	1050	1040	1045	770	480	625	60	240	290	265	26
494	502	DC-2106	790	790	790	415	620	520	66	330	310	320	41
397	442	XR-100	1120	1070	1095	650	750	700	64	285	350	320	29
350	360	XR-261	800	1000	900							100	11
352	362	XR-398	1750	1950	1850							40	2
399	444	XR-543	1130	910	1020	530	590	560	55	230	240	235	25
400	445	XR-544	930	740	835	570	600	585	70	330	320	325	39
369		XR-807	1480							70			5
394	443	XR-856	1070	440	755	70	20	45	10	50	10	30	4
		Linde											
286		X-61	970							110			11
288		X-62	1240							80			7
398		X-63	970	890	930	490	410	450	48	240	260	250	27
312		Y-1043	1100							40			4
314		Y-1044	1330							20			2

TABLE - 10 (Cont'd.)

Notes:

1. One value only.
2. P-4 primed. All others were not primed.
3. Four bonds made up each run - two tested at 70°F - one tested at 300°F - one tested at 500°F.
4. All bonds were given solvent evaporation 1 hr. at 150°F plus $\frac{1}{2}$ to 1 hr. advance cure at 300°F except sets No. 393 and 441, which were given solvent evaporation of 16 hrs. at 70°F and no advance cure.
5. All bonds were press cured at contact pressure 15 to 30 minutes at 300°F.
6. All bonds were oven cured 16 hrs. at 480°F.
7. % Thermal efficiency = $\frac{\text{Shear strength at elevated temperature}}{\text{Shear strength at 70°F.}}$

TABLE - 11

THE EFFECT OF TEST TEMPERATURE ON SHEAR STRENGTH OF DC-996 RESIN

Panel Set No: 323
Cleaning and Priming: A-1, C-1, P-4
Adhesive Composition: DC-996, 50% in xylene
Cure: 1 Press - 30 min. @ 250°F contact pressure;
Oven - 16 hrs. @ 460°F

<u>Temp., °F</u>	<u>Avg. Shear Strength, psi</u>	<u>Avg. Glue Line Thick- ness, Mils</u>
76	1430	3
100	1180	4
125	700	3
150	350	3
175	200	4
200	170	4
250	130	3

1. Prior to joining the separate panels, painted with resin, were heated one hour at 150°F to evaporate solvent and 1 hour at 300°F to "advance" the cure.

TABLE - 12

EVALUATION OF ANODIZING AS SURFACE PREPARATION OF ALUMINUM
FOR BONDING WITH RESINS

Panel Set No.	Anodiz- ing Method	Seal- ing Method	"Advance" Cure Hr. °F	Adhesive Compo- sition	Press Hr. °F	Cure Oven Hr. °F	Avg. Glue Line Mil	Avg. Shear Strength psi @°F	Bond Failure Adh% Coh%
161	E-1	(C ₆ H ₅) ₂ Si(CH ₃) ₂ 3%, dried, H ₂ O sealed	None	DC-803	1/2	250 13 300	2	Brittle	
162	"	"	"	"	"	" " " "	-	"	
163A	"	"	"	"	"	" " " "	-	No Adhesion	
354	E-1a	None	2 350	160-30- D Silicone Alkyd, oil Modified	" 300	16 480	7	1220 70	100 0
355	"	"	" "	λ-2608 Silicone Alkyd	" " " "	" " " "	7	2035 70	" "
358	"	"	" "	X-2720 Silicone Epoxy	" " " "	" " " "	5	666 70	" "
380	"	"	1/2 300	X-2608	" " " "	" " " "	0	725 70	" "
"	"	"	" "	"	" " " "	" " " "	"	120 300	" "
"	"	"	" "	"	" " " "	" " " "	<1	160 500	" "
381	"	"	" "	X-2608+ 20pts Al. dust	" " " "	" " " "	3.5	1090 70	50 50
"	"	"	" "	"	" " " "	" " " "	2	110 300	100 0
"	"	"	" "	"	" " " "	" " " "	-	90 500	" "
382	"	"	" "	DC-996	" " " "	" " " "	0.5	925 70	" "
"	"	"	" "	"	" " " "	" " " "	1	260 300	" "
"	"	"	" "	"	" " " "	" " " "	1	160 500	" "
366	"	"	1 "	"	" " " "	" " " "	4	115 70	" "
367	"	"	" "	SR-32	" " " "	" " " "	4	195 70	" "

Note: Solvent evaporated @ 150°F prior to "advance" cure (partial cure of resin before assembling bonds).

TABLE - 13

COMPATIBILITY OF SILICONE RESINS WITH SILICONE ELASTOMERS

<u>Resins***</u>	<u>10% SE-76*</u>	<u>10% Low Mol.Weight polydiphenylsiloxane*</u>	<u>10% X 6719-A*</u>
DC-801	Not compatible	Compatible	Not compatible
DC-802	"	"	"
DC-803	"	"	"
DC-804	"	"	"
DC-935	"	"	"
DC-993	"	"	"
DC-994	"	"	"
DC-996	"	"	"
DC-2103	"	"	"
DC-2104	"	"	"
DC-2105	"	"	"
XR-261	"	"	"
XR-398	"	"	"
XR-856	"	"	"
SR-17	"	"	"
SR-28	"	"	"
SR-32	"	"	"
SR-53	"	"	"
SR-61	"	"	"
SR-80	Compatible	"	Compatible
SR-82	Not Compatible	"	Not compatible
SR-98	"	"	"
SR-02	"	"	"
GE-81369	"	"	"
GE-81397	"	"	"
X-61	"	"	"
X-62	"	"	"
X-63	"	"	"
X-14-A**	"	"	"
X-14B-640**	"	"	"
X-14-C**	"	"	"
Y-1043	"	"	"
Y-1044	"	"	"

Notes:

- * Solutions in xylene. 10% SE-76 and 10% ethyl silicone gum are compatible with 10% low mol. wt. polydiphenylsiloxane.
- ** Starting materials for polymerization of resins.
- *** Solutions in xylene or toluene. Blending was done by shaking the solutions together in small test tubes. The development of cloudiness or layering was considered evidence of non-compatibility.

TABLE - 14

EVALUATION OF SILICONE RUBBER-RESIN
MIXTURES AS STRUCTURAL ADHESIVES

Panel Set No. 2	Adhesive Composition ¹	Oven Cure Hr. °F	Avg. Glue Line Thick- ness, Mils -	Avg. Shear Strength, psi. @ 70°F	Bond Failure Adh% Coh%
75	50 pts X6719-A 50 pts DC-935	16 300	6	47	50 50
271	90 pts X6719-A 10 pts DC-993 Mill mixed	" "	5	175	100 0
76	50 pts X6719-A 50 pts DC-2104	" "	Not	Compatible	
77A	90 pts X6719-A 10 pts DC-2104	" "	4	60	100 0
77B	"	" "	6	66	100 0
250	50 pts X6719-A 50 pts SR-32 Mill Mixed	" "	6	20	100 0
315	50 pts X 6719-A 50 pts SR-80	70 "	Panels fell apart - were not tested		
316	70 pts X6719-A 30 pts SR-80	" "	"	"	" " "
317	90 pts X6719-A 10 pts SR-80	" "	"	"	" " "
78	58 pts X6719-A 42 pts SR-82	16 "	No Bonds		

Notes:

1. Except where mill mixed, X6719-A was dissolved in enough toluene to facilitate blending. Blends were held at room temperature 20 to 24 hours to evaporate solvent. The mixtures were applied with a spatula.
2. All test panels were A-1 aluminum, C-1 cleaned, and P-4 primed.

TABLE - 15

THE EFFECT OF MICA FILLERS ON ROOM TEMPERATURE SHEAR
STRENGTH OF DC-996 SILICONE RESIN

Panel No. 1	Adh. Compos. DC-996 with ²	Cure @ 480°F ³	Glue Line Thickness, Mils	Avg. Shear Strength, psi, @ 70°F	Bond Failure	
					Adh%	Coh%
309	5 pts. Mica I	16 hrs.	5	1400		100
307	5 pts. Mica II	"	4	1500		"
310	5 pts. Mica III	"	4	1800		"
308	DC-996 Control	"	3	1720	100	
327	20 pts. Mica I	"	3	1500		"
328	20 pts. Mica II	"	2	1550		"
329	20 pts. Mica III	"	1	2050		"
330	DC-996 Control	"	1	2100	100	
331	50 pts. Mica I	"	4	1200		"
332	50 pts. Mica II	"	5	1400		"
333	50 pts. Mica III	"	3	1450		"
334	DC-996 Control	"	3	1700	100	

Notes:

- All panels were A-1, cleaned by Method C-1, primed by Method P-4. (Methods described in Section VI).
- Mica I = 325 Mesh White Waterground Mica, The English Mica Company, Stamford, Conn.
Mica II = Micro Mica C-3000, The English Mica Company.
Mica III = Mineralite - ground White Muscovite Mica, Mineralite Sales Corp. New York, New York

Base: 100 parts solids DC-996

- Solvent evaporated at 150°F. Resin was partially cured ($\frac{1}{2}$ hr. @ 300°F) prior to assembling the panels in bonding position.
The assembled panels in the jig were pressed 15 to 30 minutes @ contact pressure @ 300°F to "join".

TABLE - 16

THE EFFECT OF FILLERS ON HIGH TEMPERATURE SHEAR
STRENGTH OF SILICONE RESINS AND COPOLYMERS

Panel Set No. 1,4	Adhesive Composition: Resin & Filler	Avg. Glue Line Thickness, Mils			Shear Strength, psi @			Bond Failure						
		70°F	300°F	500°F	70°F	300°F	500°F	70°F	300°F	500°F	Adh% Coh%	Adh% Coh%	Adh% Coh%	
X-2608 Silicone														
Alkyd 2,3														
372	None	1	-	1	1656	-	100	100	0	---	100	0		
373	20pts Al.dust	3.5	-	2	1392	-	70	100	0	---	75	25		
374	50pts " "	4.5	-	4	1187	-	100	100	0	---	100	0		
375	20pts Mica"	8	-	8	1695	-	70	100	0	---	75	25		
376	50pts " "	2	-	1	1095	-	230	100	0	---	75	25		
377	10pts Celite	1	-	1	1407	-	140	100	0	---	50	50		
378	10pts Santocel-C	2	-	2	1002	-	280	100	0	---	100	0		
379	10pts TiO ₂	1	-	<1	1537	-	170	100	0	---	50	50		
DC-2105														
393	None	2	1	2	1040	620	250	100	0	100	0	100	0	
469	20pts Al.dust	4	4	4	735	540	390	100	0	90	10	90	10	
470	50 " " "	3.5	4	4	1160	530	340	100	0	90	10	90	10	
471	20 " Mica "	3	2	<4	1330	690	240	75	25	40	60	10	90	
472	50 " " "	4	4	3	1070	700	270	90	10	80	20	100	0	
475	10 " Celite	1	3	3	1240	440	250	100	0	50	50	90	10	
476	50 " " "	1	1	<1	850	610	310	100	0	80	20	90	10	
473	10 " Santocel-C	2	<2	<3	1155	400	220	100	0	100	0	100	0	
474	20 " " "	3.5	4	4	1130	320	260	100	0	100	0	100	0	
477	10 " TiO ₂				Hand Broken at room and high temperature									
478	50 " " "	<1	2	<1	755	510	320	100	0	90	10	100	0	
DC-804														
415	None	<1	<1	<1	840	400	300	100	0	100	0	100	0	
447	30pts Al.dust	2.5	4	5	775	370	350	100	0	100	0	100	0	
448	50pts " "	3	4	3	845	590	420	100	0	100	0	100	0	
449	20pts Mica	2	2	5	980	650	400	100	0	100	0	100	0	
450	50pts " "	<1	1	2	640	510	395	100	0	100	0	100	0	
453	10pts Celite	4	4	3	1080	890	20	100	0	100	0	100	0	
454	20pts " "	6	5	4	985	600	15	100	0	100	0	100	0	
451	20pts Santocel-C	0.5	<1	0	825	550	390	100	0	100	0	100	0	
452	30pts " "				Adhesive became flaky after cure and peeled off									
455	10pts TiO ₂	<1	2	3	610	440	270	100	0	100	0	100	0	
456	20pts " "	1.5	2	2	710	400	330	100	0	100	0	100	0	

TABLE 16 (Contd.)

Panel Set No. 1,4	Adhesive Composition: Resin & Filler	Avg. Glue Line Thickness, Mils			Shear Strength, psi			Bond Failure					
		70°F	300°F	500°F	70°F	300°F	500°F	70°F	300°F	500°F	Adh% Coh%	Adh% Coh%	Adh% Coh%
	DC-996												
406	None	3.5	2	3	1210	210	150	100	0	100	0	100	0
457	20pts Al.dust	6	7	6	905	100	100	100	0	50	50	0	100
458	50pts " "	11.5	6	12	840	150	90	100	0	75	25	0	100
459	20pts Mica	7	5	3	1215	295	210	50	50	0	100	0	100
460	50pts " "	6	5	7	1240	320	190	50	50	0	100	0	100
463	10pts Celite	14.5	14	13	1710	160	80	100	0	80	20	100	0
464	50pts "	14.5	13	13	1350	320	210	100	0	100	0	100	0
462	10pts SantocelC 3	3	3	3	1285	220	130	100	0	50	50	80	20
461	20pts SantocelC 3	3	3	6	1775	220	120	100	0	100	0	100	0
465	10pts TiO ₂	6	4	4	1690	220	90	100	0	100	0	100	0
466	50pts "	9	8	6	1430	300	120	100	0	100	0	100	0
493	None	3	4	5	1220	180	0	100	0	100	0	100	0
494	10pts Agerite	2	1	1	1735	220	20	100	0	100	0	100	0
	Alba												

Notes:

1. All panels were A-1 aluminum, C-1 cleaned, and oven cured 16 hrs. @ 480°F.
2. All X-2608 panels were P-4 primed.
3. All X-2608 panels were preheated for solvent evaporation and advance cure 1½ hrs. @ 150°F and ¼ hr. @ 300°F. All others were preheated 1 hr. @ 150°F and ¼ to 1 hr. @ 300°F.
4. Press cure at contact pressure was 30 min. @ 300°F for all X-2608 panels and 300°F until resin "flowed" for all other panels.

TABLE - 17

THE EFFECT OF CATALYSTS ON HIGH TEMPERATURE SHEAR STRENGTH OF SILICONE RESINS

Panel Set No.	Adhesive Composition: Resin + Catalyst	Shear Strength, psi @ 70°F				Shear Strength, psi @ 200°F				Shear Strength, psi @ 500°F				Avg. % Thermal Efficiency
		Runs				Runs				Runs				
		1st	2nd	Avg.	Avg.	1st	2nd	Avg.	Avg.	1st	2nd	Avg.	Avg.	
DC-955														
406	None-Control	1340	1070	1205	200	220	210	17	160	140	150	12		
407	0.5% Triethanolamine	1740	1540	1640	40	90	65	4	110	110	110	7		
408	0.5% Lead Octasol	Hand Broken												
---	0.1% Lead Octasol	550	1C				25				3			
409	0.5% Lead Uversol	200	Protein Handling				10				5			
---	0.1% Lead Uversol	910	30				0				0			
410	0.5% Iron Octasol	610	730	670	90	240	240 ¹	36	40	40	40	6		
411	0.5% Iron Uversol	390	130	260	Hand	10	10 ¹	4	0	0	0	0		
412	0.5% Zinc Octasol	1440	1000	1220	150	280	230	19	100	220	220 ¹	10		
413	0.5% Zinc Uversol	750	800	775	110	130	120	15	70	190	190 ¹	25		
414	0.5% DC-XY-15	900	500	750	20	80	80 ¹	9	0	35	35 ¹	5		
DC-804														
415	None-Control	830	850	840	400	320	360 ¹	43	340	375	360	43		
416	0.5% Triethanolamine	1010	950	980	40	580	580 ¹	59	260	350	305	31		
417	0.5% Lead Octasol	No Bond												
---	0.1% Lead Octasol	No Bond												
425	0.1% Lead Uversol	No Bond												
426	0.5% Iron Octasol	Hand Broken												
420	0.5% Iron Uversol	Hand Broken												
421	0.5% Zinc Octasol	"												
422	0.5% Zinc Uversol	"												
423	0.5% DC-XY-15	"												
424	DC-2103	"												
498	None-Control	705	1160	930	460	670	550	60	410	750	580	62		
499	1% TBT	790	1035	915	460	980	720	79	500	320	420	45		
---	1% TPT	1075				920				480				45

TABLE - 17

Penel Set No. ² Runs	Adhesive Composition: Resin + Catalyst ^{3,4}	Shear Strength, psi @ 70°F			Shear Strength, psi @ 300°F			Shear Strength, psi @ 500°F			Avg. % Thermal Efficiency	
		Runs			Runs			Runs				
		1st	2nd	Avg.	1st	2nd	Avg.	1st	2nd	Avg.		
---	507	0.5% TPT	---	1170	---	860	---	---	360	---	31	
---	506	0.5% Iron Octasol	---	200	---	120	---	---	Hand Broken	---	43	
---	505	0.5% Zinc Octasol	---	515	---	300	---	---	220	---	58	
500	504	0.5% 1:1 Zinc Octasol + Triethanolamine	225	960	960 ¹	0	440	440 ¹	40	310	310 ¹	32
393	---	DC-2105	1040	---	620	---	---	---	250	---	25	
---	468	None-Control	---	1155	---	640	---	---	---	340	---	29
---	467	1% TBT	---	820	---	720	---	---	---	430	---	52
---	488	0.5%, 5:1, Triethanol- amine + Lead Octasol	---	1120	---	495	---	---	---	440	---	13
---	489	0.5%, 5:1, Triethanol- amine + Lead Uversol	---	1285	---	260	---	---	---	170	---	13
---	490	1% TBT + 1%, 1:1, Zinc Uversol + Triethanolamine	---	380	---	400	---	---	---	100	---	26

Notes:

- From one value only.
- Four bonds comprise each panel set or run. Two tested at 70°F, one at 300°F, one at 500°F.
- Description of some of the catalysts:
Octasols--octoates-metal salts of 2 ethylhexoic acid- Harshaw Chemical Co.
Uversols-naphthenates-metal salts of naphthenic acids- " "
TBT - tetra-n-butyl titanate.
TPT - tetra isopropyl titanate.
Curing procedure as follows:
Solvent evaporation: 1 hr. @ 150°F or 16 hrs. @ 70°F
Exceptions: All DC-2103 bonds and Nos. 467, 488: 16 hrs. @ 150°F.
Advance cure: 2nd run sets containing catalysts - no advance.
Panel sets 411 through 414 in first run of DC-996 - no advance.
Remaining first, run panel sets plus control panels of 2nd run - $\frac{1}{2}$ hr. @ 300°F advance cure.
Press: All bonds except No. 417 pressed at contact pressure at 300°F until resin flowed.
Oven Cure: 16 hrs. @ 180°F. Exceptions- panel sets 467, 468, 488, 489, 490-42 hrs. @ 180°F.
5. Panel set 417 appeared unsatisfactory after advance cure and was discarded.

TABLE - 18

EVALUATION OF COMMERCIAL STRUCTURAL ADHESIVES

Panel Set No. ¹	Priming Method	Adhesive Composition	Cure ²		Avg. Glue Line thick- ness, Mils	Shear Strength psi	Bond	
			Press Min.	Oven °F Hr. °F			Failure Adh% Coh%	
52	M3C Soln.	MN3C Tape (Narmco, Inc.)	none	45 330 min	10	3000	0	100
53	None	EC-1245 (Minn. Mng. & Mfg. Co.)	"	30 250 min	6	4000	0	100
236	P-4	Armstrong A-6 with Activator "E"	60	200 None	6	825	10	90
237	"	CTL-91-D	45	325 72 300	14	1675	30	70
238	None	Scotchweld #588	75	325 None	9	2267	100	0
239	P-4	"	"	" "	6	1343	90	10
240	"	GE-SB-15 Paste	35	250 1 300	9	150	10	90
241	None	Platond	15	cold 1 300 press	6	143	0	100
242A	P-4	Synco #935 with Accelerator "N"	air dry 30	25 300 min	8	Adhesive stretches and is soft & pliable		
242B	None	"	"	" "	8	" "	"	"

Notes:

1. All test panels were A-1 aluminum, C-1 cleaned.
2. Curing procedures recommended by the manufacturers were followed.

TABLE - 19

THE EFFECT OF THE ALIGNMENT OF TEST PANELS IN DILLON TESTER JAWS

Panel Set No. ¹	Printing Method ²	Adhesive Composition	Oven Cure ³		Glue Line Thickness, Mils	Shear Strength, psi @ R.T.	Bond Failure	
			Hrs.	°F			Adh% Coh%	
202-T	P-3	X 6719-A	14	300	5	430	100	--
202-T	"	"	"	"	5	380	"	
202-T	"	"	"	"	5	400	"	
202-T	"	"	"	"	4	450	"	
202-O	"	"	"	"	5	460	"	
202-O	"	"	"	"	3	410	"	
202-O	"	"	"	"	4	370	"	
202-O	"	"	"	"	4	300	"	
203-T	"	"	"	"	5	440	"	
203-T	"	"	"	"	6	410	"	
203-T	"	"	"	"	6	400	"	
203-T	"	"	"	"	6	380	"	
203-O	"	"	"	"	3	395	"	
203-O	"	"	"	"	5	405	"	
203-O	"	"	"	"	3	360	"	
203-O	"	"	"	"	4	320	"	

1. T = Trued Alignment of Panel and Dillon Jaws with a square.
O = Dillon "off-set" as far as possible.
Test panels of A-1 aluminum, all C-1 cleaned.
2. In acetone.
3. All panels press cured at contact pressure 30 min. @ 250°F prior to oven cure.

TABLE - 20

COMPARISON OF SHEAR TEST RESULTS AT C.H.R. WITH RESULTS AT WADC

<u>Bonding Material</u>	<u>Tested at WADC</u> <u>Bond Strengths, psi</u>			<u>Tested at C.H.R.</u> <u>Bond Strengths, psi</u>		
	<u>Sample</u>	<u>@70°F</u>	<u>@500°F</u>	<u>Sample</u>	<u>@70°F</u>	<u>@500°F</u>
Shell 422-V-28 ¹ (Epoxide-phenolic resin)	A-1	1900		A-2	2050	
	A-3		1920	A-6	2100	
	A-5	2050		A-8		1750
	A-7		1760	A-10	2175	
				B-2		1300
	A-9	2160		B-4	1800	
	B-1		1380	B-6		1400
	B-3	1870		B-8	1400	
	B-5		1340	B-10		1400
	B-7	1640		C-2	2150	
	B-9		1460	C-4		1300
	C-1	2100		C-6	1850	
	C-3		1370	C-8		1200
	C-5	2100		C-10	2200	
	C-7		1370			
	C-9	2520				
	Avg.	2043	1514	Avg.	1966	1392
Avg. Deviation of C.H.R. results from those of WADC					-3.8%	-8%
X 6719-A with CHR 260 primer ²		766	273		600	
		728	273		700	
		710	182		720	
		692	173			
		575	109			
	Avg.	690	202	Avg.	673	
Avg. Deviation of C.H.R. results from those of WADC					2.5%	

Notes:

1. Samples bonded at WADC; have also been referred to as 422J in letter of 22 September 1953.
2. Samples bonded at Connecticut Hard Rubber Co.

APPENDIX

Description of Commercial Materials Used in the Research

Dow Corning

DC 40-C	Silicone Adhesive
110	Silastic Paste Adhesive
112	" " "
796	Primer, contains ethyl orthosilicate in isopropyl alcohol
801	Silicone Protective Coating Resin
802	" " " "
803	" " " "
804	" " " "
935	Silicone Electrical Insulating Varnish - Resin
993	" " " "
994	" " " "
996	" " " "
997	" " " "
1088	Silicone Insulating wire Varnish - Resin
1089	" " " "
1360	Silicone Wire Enamel Insulating Varnish - Resin
2103	Silicone bonding Resin
2104	" " "
2105	" " "
2106	Silicone Laminating Resin
X-6719A	Silicone Rubber Adhesive
XC- 270	Silicone Adhesive (pressure-sensitive type)
XC- 276	Silicone Leather-Treating Agent
XC-6708	Silicone Rubber Adhesive
XR- 100	Experimental Silicone Resin
XR- 261	" " "
XR- 398	" " "
XR- 543	" " " (Foamed Structure)
XR- 544	" " "
XR- 807	" " "
XR- 856	" " "

General Electric

81119	Silicone Oil
81369	Experimental Silicone Resin
81390	Silicone Resin (Class B insulating material)
81392	Silicone Oil
81397	Experimental Silicone Resin
SE-100	Silicone Elastomer
SF-96(500)	Silicone Oil
SF-96(1000)	" "
SM-61	Oil-in-water emulsion of a methyl silicone fluid
SR-17	Silicone flexible insulating resin for extreme hot or cold

SR-28	Silicone Resin
SR-32	" "
SR-53	Silicone Resin for water-repellency
SR-61	Silicone Resin
SR-80	" "
SR-82	" "
SR-98	Silicone Varnish, high-temp. hard flexible film resin
SR-02	Silicone Resin
SS-15	Silicone Paste for Bonding and Sealing
SS-64	Surface Preparation for Bonding and Sealing

Linde

GS-1	Silicone Resin Emulsion
X-61	Silicone Resin
X-62	" "
X-63	" "
X-14-A	Silicone Polymerization starting material
X-14-C	" "
X-14-B-640	" "
Y-1043	Silicone-styrene copolymer - experimental potting compd.
Y-1044	" "

Midland Industrial Finishes Co.

160-25-D	Clear Silicone
160-29-H	" "
160-30-D	Silicone Alkyd, oil-modified
RS-513	Silicone Alkyd
RS-556	Silicone Alkyd, oil-modified
X-2292	Silicone Phenolic
X-2605	Silicone Alkyd, oil-modified
X-2608	Silicone Alkyd
X-2720	Silicone Epoxy
V-548	Modified Silicone
V-552	" "

Connecticut Hard Rubber Co.

CHR-261	Silicone Rubber Cement
CHR-259	" " "
CHR-260	Silicone Primer Containing Silanes
G-2	Silicone oil

Monsanto Chemical Co.

Santocel-C Aerogel Silica Pigment

DuPont Co.

GS-199-S Coated Hydrophobic Silica Filler

Johns Manville

Colite-Diatomaceous Earth Silica

Cabot

Aerosil Silica - Vapor-Phase Silica

Shell

422-V-28 Epoxide-phenolic resin

WADC TR 54-98

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